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Demonstration of a Maximum Recycle Sidestream Softening System at a Petrochemical Plant and a Petroleum Refinery

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DEMONSTRATION OF A MAXIMUM RECYCLE, SIDESTREAM SOFTENING SYSTEM AT A PETROCHEMICAL PLANT AND A PETROLEUM REFINERY

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New full-scale maximum recycle sidestream softening systems at USS Chemicals, Houston, Texas and TOSCO refinery, Bakersfield, California were evaluated as a technology to achieve zero wastewater discharge. Softener process efficiency was optimum at a pH control range of 10.3 to 10.5 at 40°C and using a high mixing intensity. A problem of heat exchanger biofouling from the high dissolved organics in recycle water was effectively controlled by using Bromocide with chlorine. A total organic carbon balance over the cooling water system showed raw makeup water and process water contribute 1/3 and 2/3 of the organics, respectively. Major organic sinks were drift (60%), biodegradation (30%), and volatilization (10%). Softener sludge as analyzed for chromium by leachate tests was classified as nontoxic. Heat exchanger equipment averaged two mils/year internal corrosion. External corrosion from drift aerosols was corrected by installation of a ferrous sulfate reactor in the blow down system and improved drift eliminators in cooling towers. The TOSCO water problem of high silica and low magnesium was corrected by adding caustic and magnesium sulfate to the softener. Both plants operated satisfactorily at near zero liquid discharge. Operating costs and benefits are discussed.

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FOREWORD

EPA is charged by Congress to protect the Nation's land, air, and water systems. Under a mandate of national environmental laws focused on air and water quality, solid waste management and the control of toxic substances, pesticides, noise, and radiation, the Agency strives to formulate and implement actions which lead to a compatible balance between human activities and the ability of natural systems to support and nurture life.

The Robert S. Kerr Environmental Research Laboratory is the Agency's center of expertise for investigation of the soil and subsurface environment. Personnel at the Laboratory are responsible for management of research programs to: (a) determine the fate, transport and transformation rates of pollutants in the soil, the unsaturated zone and the saturated zones of the subsurface environment; (b) define the processes to be used in characterizing the soil and subsurface environment as a receptor of pollutants; (c) develop techniques for predicting the effect of pollutants on ground water, soil and indigenous organisms; and (d) define and demonstrate the applicability and limitations of using natural processes, indigenous to the soil and subsurface environment, for the protection of this resource.

Zero discharge technology is the final goal for development and implementation of reuse/recycle water systems at industrial plants. Quality data is needed to support regulation, enhance technology transfer, and encourage acceptance of such feasible systems. The research report presents results of a recycling cooling water system study for two different industrial processes. Topics covered are (1) performance optimization, (2) impact of recycle streams, (3) fate of organic contaminants, and (4) sludge toxicity.

Clinton W. Hall
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ABSTRACT

The purpose of this project was to document the performance of a maximum recycle, sidestream softening system at the USS Chemicals Petrochemical Plant in Houston, Texas. The concept was to reuse all effluent streams as makeup to the cooling water system, with one exception--the demineralizer regeneration water. A blowdown from the cooling water system was processed through two precipitation softeners to remove the potential scale-forming constituents and returned. Thus, the plant approached zero liquid discharge.

The system was started up in November 1979, concurrent with the demothballing of the ethylene unit. The styrene unit had been in continuous operation. In May 1980, the research effort was commenced. There were many problems with the new, innovative system. Consequently, much of the effort involved direct interaction in improving the system.

The most significant efforts involved the control of biofilm formation in an extremely high organic concentration cooling water; the enhanced performance of the precipitation softeners; the evaluation of the toxicity of the softener sludge (and its subsequent delisting as a toxic material); and the delineation of an emergency blowdown system.

There are many things yet to be learned in this very applied area of research. Hopefully, this document can be used as an example of the successful application of precipitation softening to maximize water recycle; and that many of the advances made can be applied to new system.

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Section 1

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INTRODUCTION

Our national goal, as promulgated by Congress, is to eliminate pollution from industrial facilities within the decade of the 1980s [1]. At first glance, this "zero pollution" goal appears to be an expensive, hypothetical idea difficult to obtain. In reality, however, the technology to attain this goal is already being developed and can be implemented.

At the forefront among techniques to eliminate wastewater pollution is sidestream softening. Since cooling tower blowdown accounts for the single greatest source by volume of all types of industrial water discharges (over 1 trillion gallons per year)[2], application of sidestream softening to achieve zero discharge constitutes a major reduction in industrial water pollution.

Sidestream softening treats a portion of the cooling water in a lime softener, then returns the treated water to the cooling system. The softener precipitates scale-forming materials from the cooling water as a sludge which can be dewatered and landfilled. This allows cooling water to be recirculated indefinitely without the normally necessary effluent discharge. Other plant waste streams may also be added to the softener sidestream, resulting in further reduction of aqueous discharge, Thus it is quite possible to attain a true zero discharge operation with sidestream softening.

In addition, the chemicals involved in the softening reaction (lime and soda ash) are relatively inexpensive and the theory of softening is well understood. Because of these benefits, at least 20 plants in the United States currently use sidestream softening to attain zero discharge.

The incentives to industry for the construction and operation of a zero blowdown or discharge sidestream softening system have been both regulatory and economic in nature [3, 4]. Because of the EPA effluent limitations for chromium and zinc, operational requirements are either blowdown treatment or a switch to alternate corrosion inhibitors. Since chromate is widely recognized as the best corrosion inhibitor for cooling water systems, zero discharge sidestream softening is often the method of choice. It allows for the continued use of chromate in higher concentrations than permitted within discharge limitations. Depending upon the costs of water, pretreatment, and wastewater treatment in a given industry, sidestream softening could provide operating cost savings which yield a capital payback period of about five years. In some arid regions of the country, this type of water reuse may emerge as the only economical alternative.

Although the concept is simple, a cost-effective process design and cooling water treatment program requires meticulous selection. High levels of total dissolved solids (TDS) from increased cycles of concentration significantly affect the chemistry of both the softener and the cooling water. Also, interactions between chemicals added to the cooling and softening systems can be detrimental to the proper function of each.

The practical design information obtained is documented as follows:

1. Development of zero discharge sidestream softening technology;
2. Basic criteria used to determine the suitability of various sidestream softening techniques;
3. Example of design application in a "zero" or minimum aqueous discharge system at the USS Chemicals installation in Houston, Texas;
4. Improvements of the system based on experimental results during its start-up and operation.

Section 1 of the report contains a history of the development of zero-discharge sidesream softening, a description of the USS Chemicals plant, and the sidestream softening system. Section 2 illustrates the basis for sidestream softening design, and provides the background for the case studies which make up the rest of the report.

Section 3 documents the zero-discharge sidestream softened cooling tower system at USS Chemicals. Raw data assembled in tabular form in the Appendix can be used as a basis for further research. Section 4 shows the results of experiments concerning specific aspects of the USS Chemicals sidestream softening operation, designed to optimize the softening process.

Section 5 describes experiments with the biocides used to control biological fouling in the heat exchanger system. The need to blowdown periodically is addressed in Section 6, with in the areas of chromate precipitation; and the landfill disposal of chromate-bearing sludge. Section 7 deals with accounting for the organic material entering and leaving the cooling water system. Section 8 gives an evaluation of the costs of the zero-discharge sidestream softening system.

GENERAL CONCLUSIONS

The sidestream softening concept was particularly attractive to USS Chemicals because the cost of their water was relatively high, the efflent discharge regulations were tough, and they wanted to continue to use chrome and zinc as corrosion inhibitors in the cooling water system. Prior to the installation of a sidestream softening, USS Chemicals had only a rudimentary (physical, chemical solids removal) wastewater treatment system.

The decision to minimize blowdown was made in the mid-1970's. The economics of sidestream softening were the most advantageous, especially when viewed as a preinvestment to facilitate compliance with future regulations. The fact that the plant approaches zero discharge would minimize expenses in the future.

The major initial problems encountered at USS Chemicals were the microbiological fouling in the cooling water system and high sludge disposal costs because of the original classification as toxic. Both problems were resolved satisfactorily during the course of this research.

The major problem that was unresolved during the study phase of the project was drift loss from the cooling towers. The drift with the concentrated dissolved solids deposited on equipment and pipelines with a 50-foot radius of the towers and created an external corrosion problem. At one point, solids from the drift accumulated on a transformer and shorted it out. Plant personnel then started using an improved coating on the equipment to mitigate the problem and the transformer is cleaned every six months.

Finally, in June 1981, USS Chemicals rebuilt the largest ethylene cooling tower and installed high efficiency drift eliminators. As expected, the TDS concentration in the cooling water system increased (roughly 50 percent). In September 1982, the styrene plant was mothballed due to poor economic conditions. This move further increased TDS levels in the ethylene cooling tower, which approached 30,000 mg/L. In December 1982, USS Chemicals installed the chrome destruction blowdown system researched in Section 6. They are now blowing down at low flow (5 gpm) to decrease the TDS concentrations in the cooling water to more reasonable levels.

The project demonstrated that a cooling water system could be used as a sink for wastewaters, and that a softening system installed as a sidestream could control scaling. To the many industrial plants which currently employ cooling water systems as a basic utility, sidestream softening offers an opportunity to maximize reuse of industrial cooling water.

In the TOSCO case the design, startup, and operation was smooth from the beginning. Microbiological problems were minimized because no recycle streams with organics were introduced into the cooling water system.

TOSCO was unique in the use of caustic instead of lime in the softener; and in the use of magnesium sulfate to remove silica from the cooling water. Also, dissolved solids were in the low range, and no external corrosion due to drift deposition was observed.

As a footnote, the TOSCO refinery was shut down in early 1984 for economic reasons associated with the price of gasoline.

Recommendations for Further Study

This initial attempt to demonstrate the technology of a minimum blowdown system also served to improve sidestream softening process performance. Nevertheless, as with most scientific efforts, the research only serves to multiply the questions. In some order of priority, the following tasks need to be performed:

1. Development of a design methodology that can take into account the various process options;
2. Determination of the impact of the high dissolved solid level on calcium carbonate, magnesium hydroxide, and silica adsorption in the softening reaction.
3. Investigations into the best types and optimum concentrations of scale inhibitors in sidestram softening systems.
4. In-depth economic analyses of sidestream softening systems.
5. Evaluation of the various softening options.

In addition, much work could be done to quantify the environmental effects of sidestream softening as a minimum discharge strategy.

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SECTION 1

THE DEVELOPMENT OF ZERO DISCHARGE SIDESTREAM SOFTENING

A common cooling water system consists of a cooling tower, conveyance system, and heat exchangers. Heat is transferred through the metal tubes of the heat exchanger into the water. The water is cooled in the cooling tower, then returned to the exchangers. Heat exchange requirements determine the makeup water flow rate.

BLOWDOWN AND ZERO-DISCHARGE SYSTEMS

A major problem in recirculating systems is that evaporation concentrates dissolved solids in the cooling water to levels at which scaling occurs on heat exchange surfaces. Therefore, a purge stream (blowdown) is continuously maintained to limit the maximum concentrations of certain dissolved species in the system. A cooling water system schematic is shown in Figure 1-1. Source or "makeup" water is pumped into the cooling tower basin to replenish losses from evaporation, blowdown, and drift.

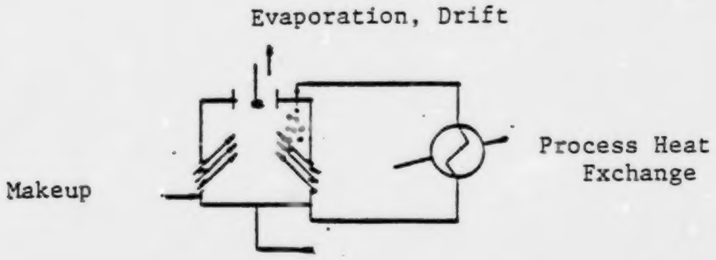

Figure 1. Typical induced-draft open recirculating cooling tower.

In addition, a variety of chemicals may be added to the cooling water to prevent scaling and corrosion. Chromium (in hexavalent form) and zinc inhibit corrosion. Polyphosphates and phosphonates and other microbiocides minimize microbial fouling. When used, these chemical additives are also discharged in the blowdown.

Some recirculating systems are closed to the atmosphere: cooling is by sensible heat transfer alone, through air fins analogous to an automobile's radiator. Other cooling water systems, such as the existing once-through systems in which no cooling tower is necessary. Many once-through systems are now required by federal law to convert to recirculating systems in order to reduce thermal discharges.

Some cooling water discharges from recirculating cooling towers contain chrome and zinc, which can be toxic to aquatic life. Effluent standards currently call for concentrations of hexavalent chrome in the range of 0.02 mg/L, and zinc below 0.5 mg/L. The phosphorus in blowdown is a potential eutrophication agent. Constituents of chlorine and microbiocides may also be toxic to the environment. Heat and high dissolved solids levels enhance additional environmental problems.

The zero-discharge recirculating cooling system solves the problem of toxic discharge by continuously recirculating the cooling water with only minimal discharge. The zero discharge system removes deleterious materials by softening, demineralization, or some other form of advanced treatment. A technology actively under consideration (including ion exchange, reverse osmosis, and electrodialysis), lime/soda softening of a cooling water sidestream is economically attractive and the most highly developed.

The sidestream softening process (Figure 1-2) removes the principal scale-forming agents of calcium, magnesium, and silica. Lime is added to raise the pH to 10.5 - 11.0 where ionic bicarbonate is converted to ionic carbonate, which reacts with ionic calcium to precipitate out as calcium bicarbonate. Dissolved silica is removed by adsorption onto magnesium hydroxide, which precipiates as floc and is removed in the softener settler. The treated water is then clarified, filtered, and its pH is adjusted for return to the cooling tower.

EARLY SIDESTREAM SOFTENING RESEARCH

The concept of integrating a softening unit into a cooling water system to achieve zero discharge was originated by Fowlkes in the late 1960s at Union Carbide's Oak Ridge Gaseous Diffusion Plant (Oak Ridge, Tennessee) [1]. Proposed regulations for effluent to the Clinch river severely restricted chromate discharges. The corporation did not want to discontinue the use of superior chromate-bearing corrosion inhibitors, or to treat the blowdown prior to discharge.

Originally, blowdown was to be blended into two existing makeup water softeners. The blowdown water could be successfully softened by laboratory jar tests. A one-year operational test was conducted in 1969, then continued for another 1 1/2 years. Corrosion rates were monitored with bare steel and copper coupons. Rates were below 1 mpy (mill per year). They were comparable to previous rates in the system.

The Oak Ridge cooling water system processed about 12 MGD makeup water. Fifteen percent of this makeup water flow was blown down and recycled to the makeup water softeners. A bleed to the firewater system reduced the TDS

TABLE 1-1. Oak Ridge Water Quality Data (1, 2, 3)

Parameter	Makeup	Operating	Test Loop
Calcium Hardness as $CaCO_3$	72	179	959
Magnesium Hardness as $CaCO_3$	38	161	519
Sulfate as SO_4	62	487	2345
Dissolved Solids	170	1106	4869
Chlorides as Cl		59	647
Silica as SiO_2		23	111

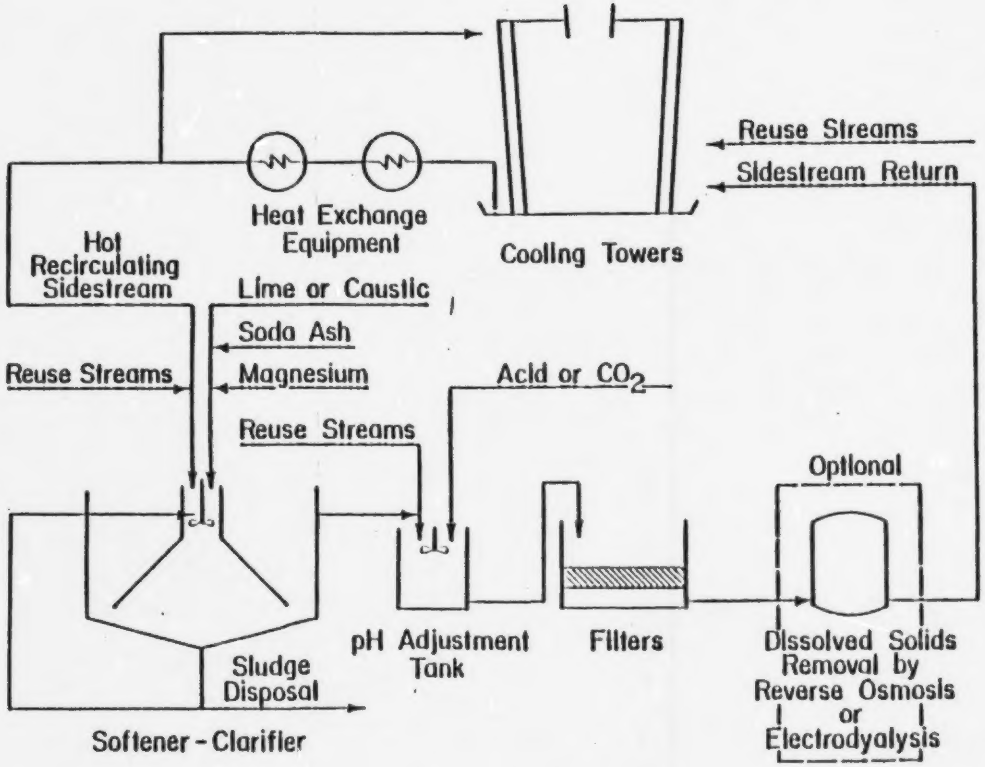
Reuse Streams
Sidestream Return
Heat Exchange Equipment
Cooling Towers
Hot Recirculating Sidestream
Lime or Caustic
Soda Ash
Reuse Streams
Magnesium
Acid or CO2
Reuse Streams
Optional
pH Adjustment Tank
Filters
Dissolved Solids Removal by Reverse Osmosis or Electrodyalysis
Sludge Disposal
Softener - Clarifier

Figure 1-2. Sidestream softening system with optional demineralization

TABLE 1-2. Feasibility Tests of a Sidestream Softener for Oak Ridge (2)

Parameter	Softening	After 104°F (60°C) Softening
pH	6.55	9.70
"M" Alkalinity (as $CaCO_3$) ppm	7	76
Total Hardness (as $CaCO_3$) ppm	566	80
Calcium (as $CaCO_3$) ppm	364	22
Sulfate (as SO_4) ppm	737	725
Dissolved Solids ppm	1440	1474
Silica (as SiO_2) ppm	36	9.5

Note: Feed rates: 150 ppm lime and 640 ppm soda ash level from a calculated 4000 mg/L to actually 1100 mg/L. Fowlkes set up a test loop without a firewater bleed [2] to measure corrosion rates for the true zero discharge situation. He found that corrosion rates were higher, but tolerable. The qualities of the makeup water, actual cooling water, and test loop water are shown in Table 1-1. Fowlkes also tested the concept of a separate softener for blowdown treatment. This took advantage of a hot water temperature and the high concentration gradients of the reactants [3]. The tests results were encouraging (Table 1-2). The separate softener was installed in 1974.

The Oak Ridge facility was still operational in June 1978 in the redundant mode (i.e., with both front-end and sidestream softeners). A low pH (6.4-6.5) has been maintained in the recirculating water system. The performance of this softener system [4] has been a successful scaleup of the earlier laboratory feasibility tests.

In 1973 Crits and Glover investigated sidestream treatment for a 50 MW electric utility [5]. They recommended a higher pH control (7.5-8.5) for their recirculating water system compared to Fowlkes. Control limits were established for all the scaling and corrosive materials, which included silica. Their sidestream softening process was boosted from five to 30 the cycles of concentration of the cooling water. This was a remarkable increase of 600 percent.

Crits and Glover later reported that the optimal sidestream configuration to achieve zero discharge consisted of a softener followed by a reverse osmosis module to control TDS not removed in the softener [6]. They reported that such a system could be economically applied to any tower operation. However, capital and operating costs of lime softening were much less than for reverse osmosis and ion exchange processes. Suspended solids, silica, and calcium/magnesium precipitation could limit recovery by the reverse osmosis system, and foul ion exchange resins.

In 1975, Matson and Perry performed a pilot study for sidestream softening of a petrochemical plant cooling water system [7, 8]. Treated effluent was added to the makeup of the cooling water system. Sidestream softener then treated roughly half the makeup water flow. The pH in the system was controlled by carbon dioxide added to the water. This eliminated sulfate ions present from sulfuric acid treatment. Bicarbonate alkalinity was conserved, thereby minimizing the soda ash requirement in the sidestream softener. Results from the lime softening loop pilot test (Table 1-3) indicated that the water was supersaturated by carbon dioxide and held the high bicarbonate alkalinity at a reasonable pH [9]. The technical limitation for the system was calcium carbonate scaling potential.

Some problems were detected in testing the feasibility of the system but none insurmountable. Chemical additives such as phosphonates and polyphosphates interfered with the softening process, so use was discontinued. Silica levels were effectively controlled with the addition of magnesium oxide powder to the softening reactor. The plant at which the plot tests were conducted was modified to achieve zero blowdown with lime softening, and is the subject of the study [10].

TABLE 1-3. Recirculating Water Quality in Pilot Plant Using Carbon Dioxide for pH Control, (9)

Parameter	River Water	Recirculating Cooling Water
Calcium hardness, in milligrams per liter as $CaCO_3$	95	290
Magnesium hardness, in milligrams per liter as $CaCO_3$	10	51
Total alkalinity, in milligrams per liter as $CaCO_3$	105	247
Total dissolved solids, in milligrams per liter[a]	240	4800
Nonhardness TDS[b] in milligrams per liter	135	4520
Total suspended solids, in milligrams per liter	50	70
Silica, in miligrams per liter	9	20
Chrome (hexavalent, in milligrams per liter)		29
Zinc, in milligrams per liter		2
Total hardness exiting softening loop	155 mg/L as $CaCO_3$	

[a] Sum of hypothetical compounds in solution
[b] TDS, less calcium and magnesium

A high-density solids contact unit for sidestream softening [11] was developed by Frazer in 1975. The unit recycled precipitated solids to the reaction zone in a relatively small volume of water. This allowed the reactions to occur in the presence of 50 g/L of dry solids. Frazer also advocated the use of a two-stage treatment at high TDS levels to remove magnesium in the first stage, and remove calcium in the second stage.

In 1977, Darji reported on the advantages of the high density solid process for sidestream softening [12]. His case studies involved electric power generation plants with poor quality makeup water. Darji indicated that makeup softeners were workable in conjunction with sidestream softeners if a plant's service water also required softening. He recommended two-stage softeners followed by a filter for suspended solids removal for the sidestream configuration.

Webb in 1975 made an economic evaluation of sidestream softening to achieve zero discharge at a coal burning electric power generating plant [13]. He compared six different options, combining pretreatment of river water versus no treatment; sidestream softening versus blowdown recovery by brine concentration; and a sidestream treatment with and without recarbonation. His least cost option was untreated river water makeup with sidestream softening and recarbonation. In the analysis, the size of the evaporation pond was the critical factor. It was smallest in the least cost case. Webb's sidestream treatment had two stages: magnesium removal by addition of caustic (NaOH) in the first stage and calcium removal by the addition of lime ($Ca(OH)_2$) in the second stage. Soda ash was not added in Webb's theoretical model; therefore, a very high bicarbonate alkalinity was needed in the cooling water. Conclusions were that sidestream softening treatment would achieve zero discharge.

Rice summarized the variety of process schemes for eliminating blowdown. They included reverse osmosis, vapor compression, and solar ponds in steam/electric power plants [14]. He acknowledged that most of the schemes included the use of a sidestream warm lime treatment. For systems that required further TDS removal prior to sidestream recycling, effluent from the lime treatment process was the logical source of water supply. It was clarified, free of colloidal silica, and greatly reduced in organic matter. In the economic analysis, schematics included the sidestream lime softener as an integral part of the process for achieving zero discharge (e.g., Figure 1-3).

Wirth and Westbrook also considered the zero discharge concept for the electric power industry [15]. Their generalized system consisted of chemical (lime-soda ash) softening, filtration, and brine desalting. They investigated the optimum salinity for a given recirculating cooling water. All their schemes included the use of a sidestream softener. Their economic analysis showed that the combination of sidestream softening and electrodialysis had the lowest overall capital requirements. They concluded that such a combination was ideal in an optimum salinity region to achieve the necessary calcium, silica, and overall salt removal from the system.

A pilot test program using sidestream softening as a means to achieve

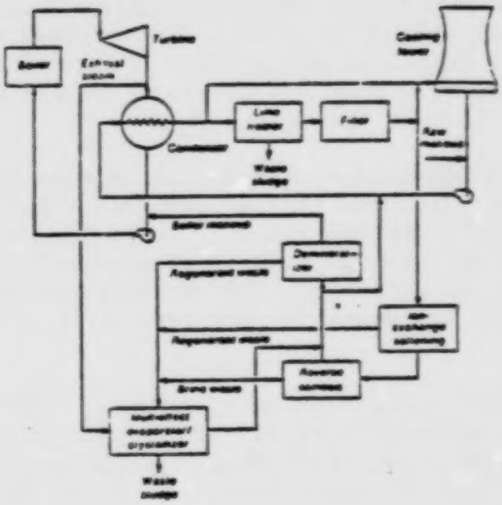
Turbine
Cooling tower
Boiler
Exhaust steam
Condenser
Filter
Waste sludge
Boiler makeup
Demineralizer
Regenerant waste
Ion exchange softening
Regenerant waste
Reverse osmosis
Brine waste
Multieffect evaporator/crystallizer
Waste sludge

Figure 1-3. Sidestream water treatment plant (Rice).

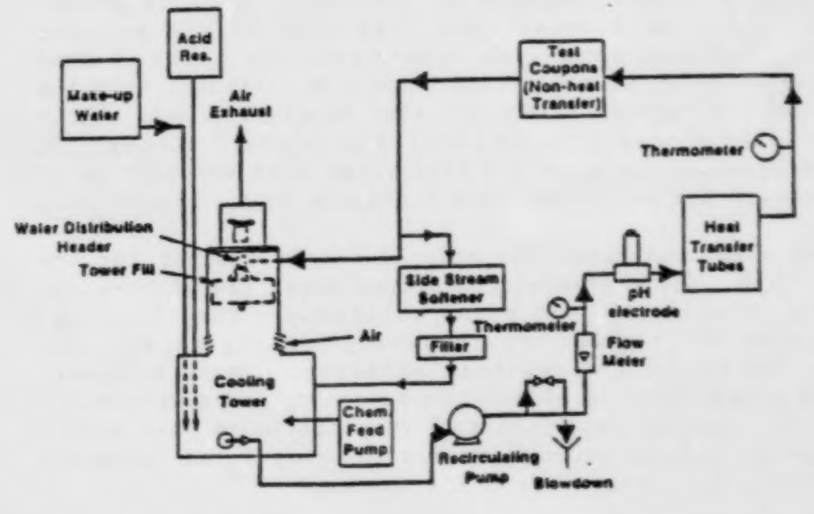
Acid Res.
Make-up Water
Air Exhaust
Test Coupons (Non-heat Transfer)
Thermometer
Water Distribution Header
Tower Fill
Heat Transfer Tubes
Side Stream Softener
pH electrode
Thermometer
Air
Filter
Flow Meter
Cooling Tower
Chem. Feed Pump
Recirculating Pump
Blowdown

Figure 1-4. Pilot Cooling Tower with ZBD capability (Reed, et. al.).

zero blowdown was reported by Reed et al. [16]. A sophisticated pilot cooling tower (Figure 1-4) was constructed and tested an ultra-high TDS recirculating water level of the type expected by zero blowdown systems currently under design. Reported corrosion rates of stainless steel and copper alloy specimens were low--less than 2 mpy. Specific detail of the test conditions was not provided. The performance of the system depended on the TDS level, the mechanical operations, and the various cooling water treatments applied. They concluded that zero blowdown employing a sidestream lime softening process would be workable for both new and existing cooling tower systems.

RECENT DEVELOPMENTS

In 1977, Hennings et al reported on a sidestream softening system that had been operating since 1976 at the Georgia-Pacific petrochemical plant in Plaquemine, Louisiana [17]. A schematic of the system in shown in Figure 1-5. As at Oak Ridge, the concept evolved from the successful recycling of blowdown to makeup water softeners. Four independent cooling towers were connected into a common circuit. A single sidestream softener served the system.

Corrosion rates in the cooling water system were reported to be less than 1 mpy. Typical cooling water quality is shown in Table 1-4. Microbiological problems were minimal, probably because the sidestream softener acted as a disinfection process and chlorine was conserved through the system. Precipitation was not a problem. Hennings concluded that the sidestream softening concept was the most economic choice for their plant to meet environmental standards. Deutsch [10] indicated that the plant was successfully operating in the zero discharge mode as of February 1979.

Recently, Curtis did an economic analysis of sidestream softening for a petrochemical plant [18]. He compared its costs to expenditures actually incurred in conventional (i.e., discharge) cooling water operations. Zero discharge sidestream softening offered substantial savings by conserving cooling water chemicals, eliminating blowdown treatment, and cutting makeup water requirements by 20 percent. These savings equaled the total amortized cost of the sidestream softening system. After-tax savings were estimated at $100,000 using sidestream softening for the period 1980-2000, with a return on investment of 12 percent. Curtis concluded that sidestream softening was breakeven based on current economics, but became positively attractive when environmental regulations and/or water conservation forced the issue.

In August 1978, Southern California Edison brought on-stream its Coolwater electric power generation plant, with both front-end and sidestream softeners designed into the cooling water system [19]. The makeup water was from the underground Mojave River. EPA mandated that no aqueous effluents were to be discharged. The actual makeup water quality was better than expected. Also, the front-end softeners were not needed. In October 1978, the cooling water system was running at about 3,000 mg/L TDS. This was far below the expected steady state of 15,000 mg/L. Apparently, the heat load was less than expected to evaporate enough water to concentrate the TDS to the expected values. In Table 1-5, the water quality for the plant is shown.

A number of interesting features differentiate this Coolwater facility from other sidestream softening systems. Instead of lime, NaOH was added to the softening reactor for pH control. It was cheap, easy to store, and was simpler to feed to the reactor. Powdered magnesium oxide was added to ensure sufficient silica removal. Such operational control maximized bicarbonate alkalinity in the recirculating water and allowed pH control close to the calcium carbonate solubility limits. The soda ash requirement for the softening process was reduced about 100 mg/L.

Five plants utilizing the sidestream softening concept that have been reported on in the literature are as follows:

1. Oak Ridge (DOE) (TN)
2. Georgia-Pacific (LA)
3. S.C. Edison, Coolwater (CA)
4. Martin Drake Power (CO)
5. USS Chemicals (TX)

The Martin Drake Municipal Power Plant has operated in the sidestream-softener mode since July 1978. USS Chemicals (formerly Arco Polymers, Inc.) went onstream in the fourth quarter, 1979. It differs from other plants in that carbon dioxide is used to control cooling tower pH. Also, cooling tower makeup includes both process effluent and rainfall runoff. This enhances the system's recycle capabilities. See Figures 1-6 through 1-11 for photographs of the facility.

In May 1980, the U.S. Environmental Protection Agency funded the two-year study of the USS Chemicals sidestream softening system which is this final report. Operational data collected during the project period is discussed in this report. A number of experiments designed to optimize various aspects of the zero discharge cooling system are also noted.

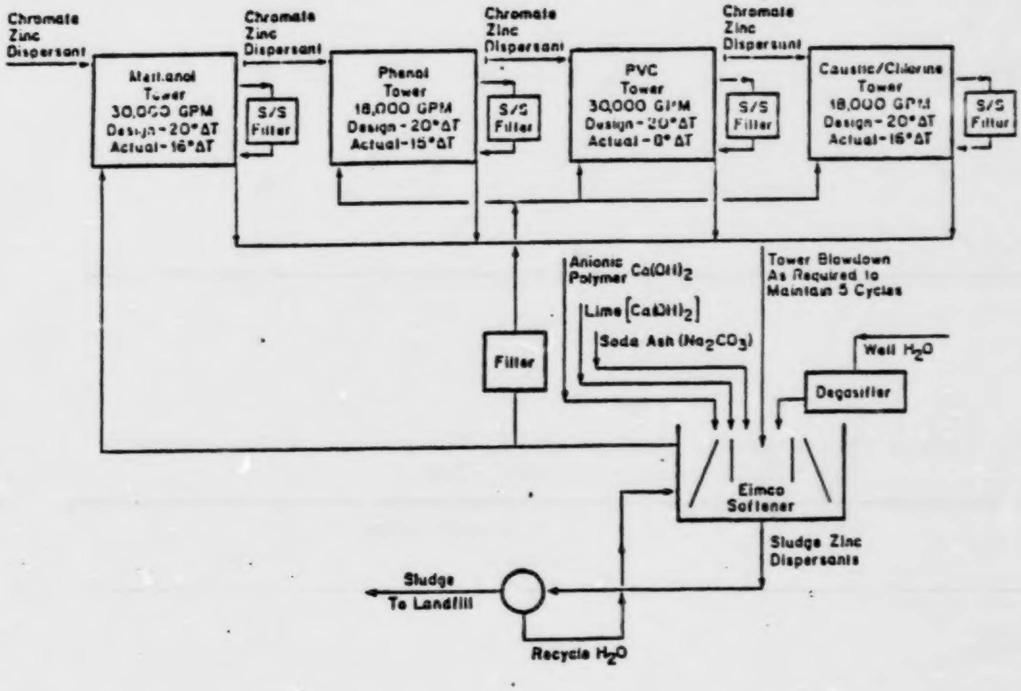
Chromate Zinc Dispersant
Methanol Tower 30,000 GPM Design - 20°ΔT Actual - 16°ΔT
Chromate Zinc Dispersant
S/S Filter
Phenol Tower 18,000 GPM Design - 20°ΔT Actual - 15°ΔT
Chromate Zinc Dispersant
S/S Filter
PVC Tower 30,000 GPM Design - 20°ΔT Actual - 8°ΔT
Chromate Zinc Dispersant
S/S Filter
Caustic/Chlorine Tower 18,000 GPM Design - 20°ΔT Actual - 16°ΔT
S/S Filter
Anionic Polymer
Ca(OH)2
Lime [Ca(OH)2]
Soda Ash (Na2CO3)
Tower Blowdown As Required to Maintain 5 Cycles
Filter
Well H2O
Degasifier
Eimco Softener
Sludge Zinc Dispersants
Sludge To Landfill
Recycle H2O

Figure 1-5. Georgia-Pacific sidestream softening.

TABLE 1-4. Recirculating Water Quality at Georgia-Pacific (17)

Parameter	Concentration (mg/L)
pH[†]	6.5
TDS	8000
Total Hardness	480
Calcium	141
Magnesium	31
Chloride	650
Sulate	4500
Sodium and Potassium	2648
Silica	40
Bicarbonate	56
Total Alkalinity	46

[†] Unitless

TABLE 1-5. Actual Versus Design Recirculating Water Quality Parameters for S.C. Edison Coolwater Plant

Parameter	Concentration (mg/L) Actual	Design
Calcium as $CaCO_3$	800	300
Magnesium as $CaCO_3$	100	300
Alkalinity as $CaCO_3$	50	150
Sulfates	1300	†
Chlorides	300	†
Silica	50	150

[†] Not given

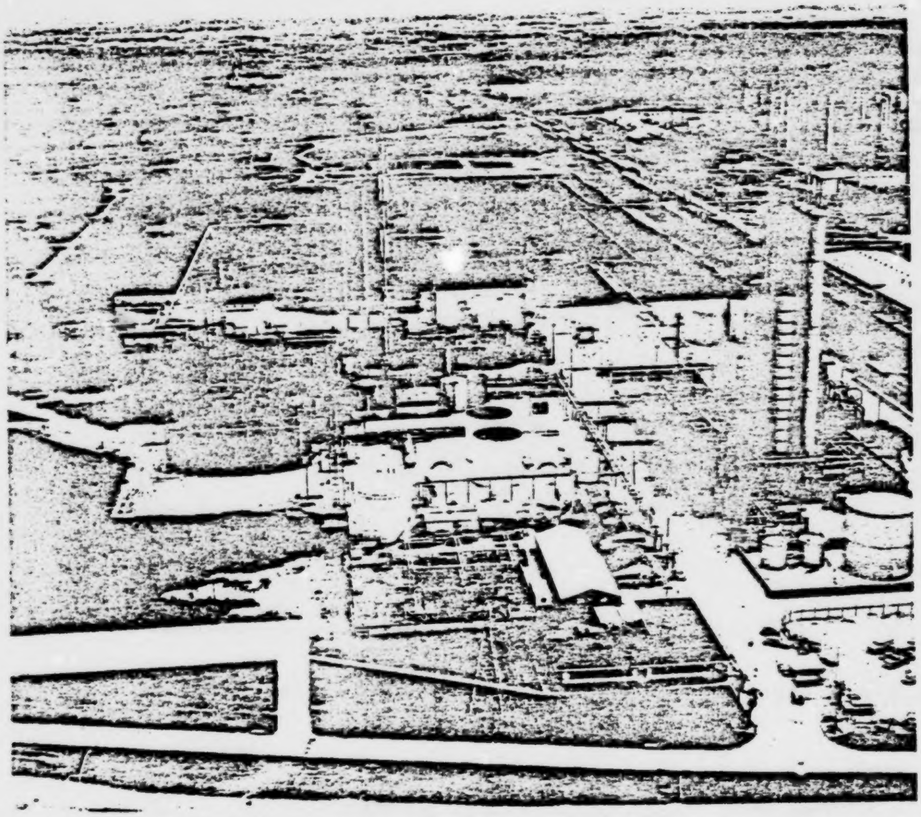

FIGURE 1-6. View of the USS Chemicals ethylene and styrene petrochemical plant.

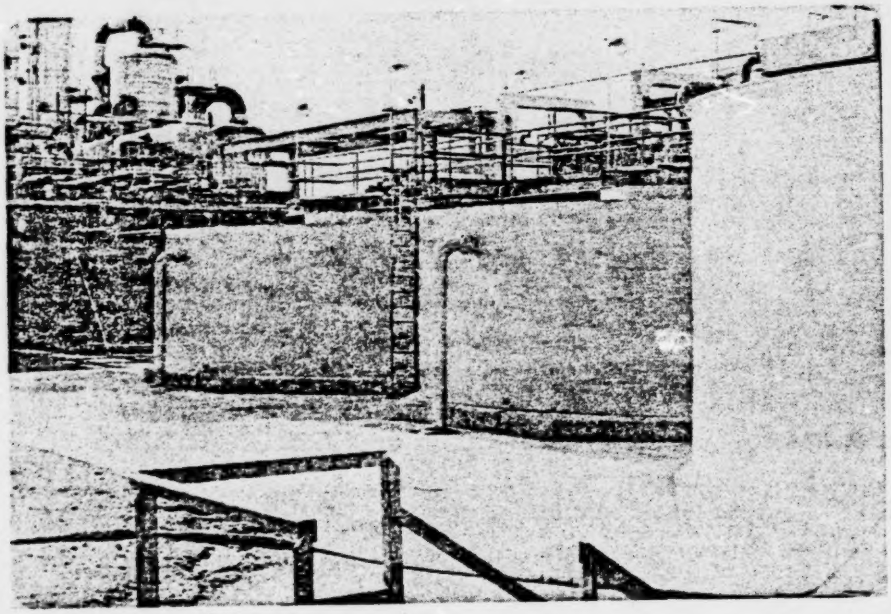

FIGURE 1-7. Side view of the two sidestream softeners.

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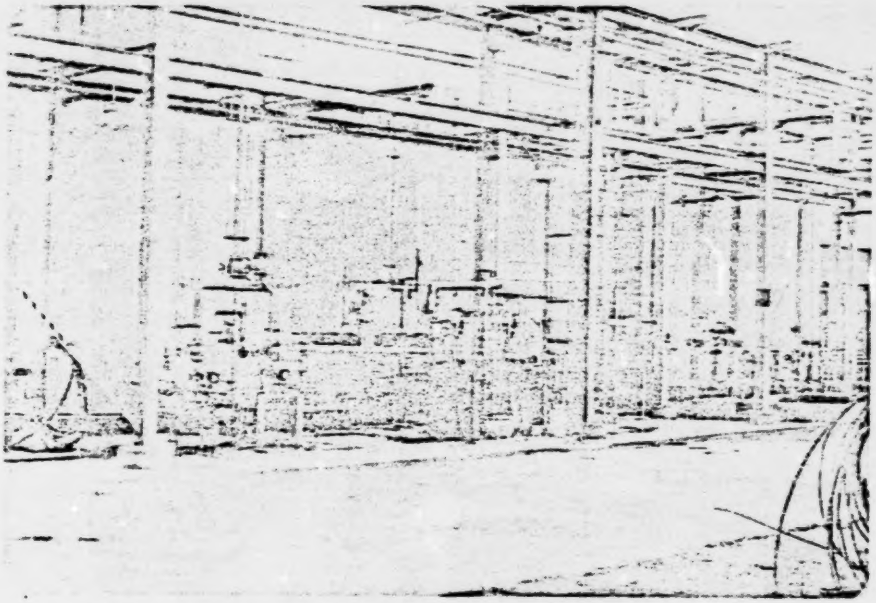

FIGURE 1-8. View of softeners and soda ash delivery system.

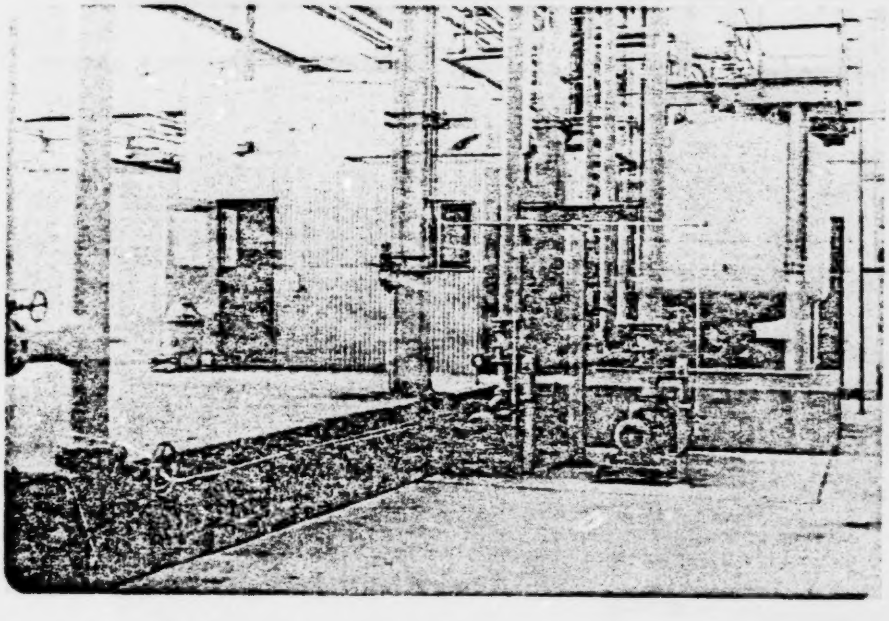

FIGURE 1-9. Control room and filters.

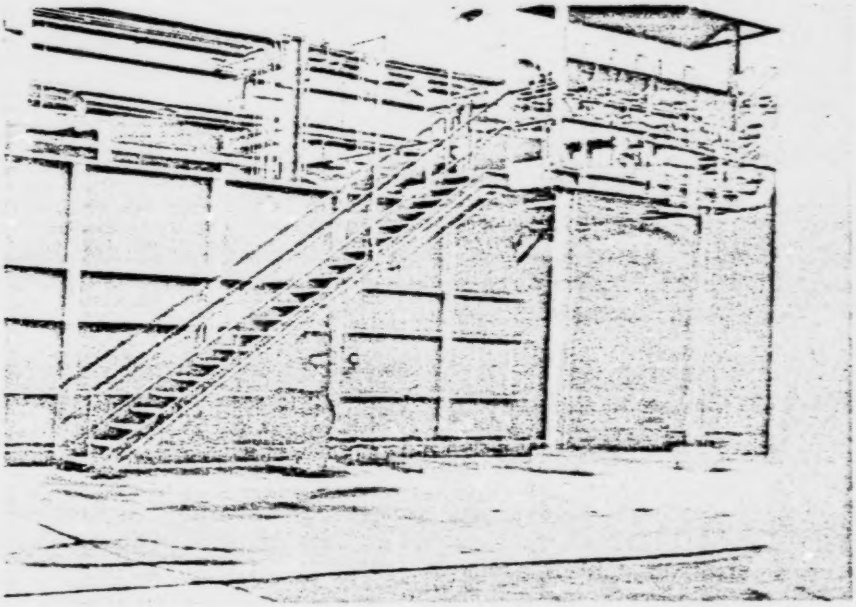

FIGURE 1-10. Side view of recarbonator.

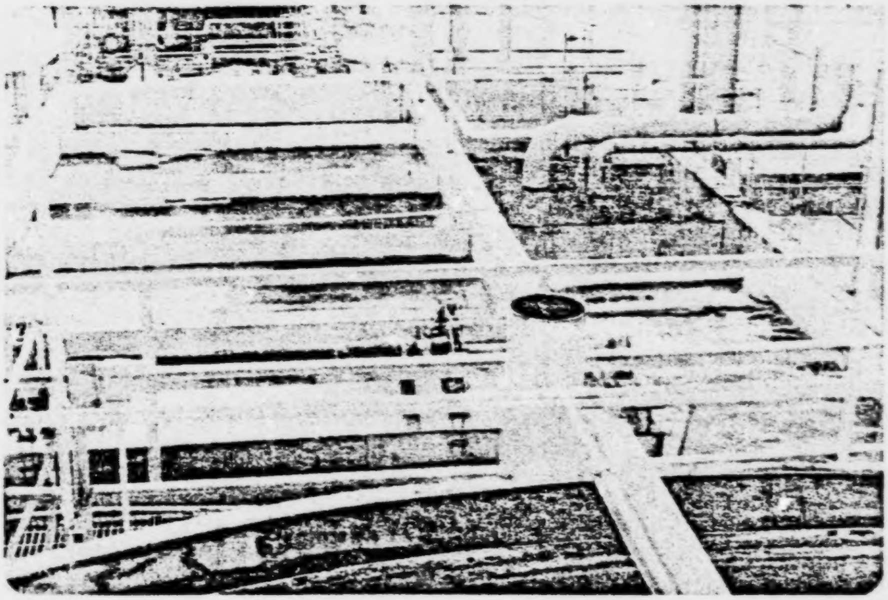

FIGURE 1-11. Top view of recarbonator.

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SECTION 2

SIDESTREAM SOFTENER DESIGN

The zero discharge sidestream softening system includes the following processes:

(1) A softener (solids contact reactor/clarifier) to remove scale-forming elements.

(2) A pH adjustment tank to acidify the treated water to the proper cooling water pH.

(3) Gravity or sand filters to remove any suspended particles.

An optional unit process can be added after the filters to reduce the total dissolved solids (TDS) concentration, e.g.,

(4) electrodialysis or reverse osmosis unit.

Such a unit may be warranted for the control of chloride which is corrosive at very high concentrations ($>$ 10,000 mg/L).

Scale-forming materials which are removed by the softening reaction are calcium and silica. They precipitate as calcium carbonate and calcium sulfate ($CaCO_3$ and $CaSO_4$) and silica dioxide (SiO_2) respectively. Calcium, the most prevalent scale-forming element, is removed at the high pH in the softener as calcium carbonate. Dissolved silica is removed by adsorption onto magnesium hydroxide floc which precipitates at pH's $>$ 9.0.

Lime (CaO) or caustic (NaOH) is added to the softener reaction zone to raise the pH. The selection is based on cost: lime is usually cheaper, but it produces more sludge than caustic. Soda ash is required when insufficient carbonate (CO_3^{2-}) is available to precipitate the calcium. If silica scale is the controlling constituent, then magnesium can be added to remove it. Suitable sources of magnesium are magnesium oxide, magnesium sulfate, magnesium chloride or dolomitic lime.

The objective of the preliminary design process is to specify the softener size, sidestream flow rate, and the rate of addition of chemicals necessary to maintain the quality of the recirculating cooling water within the required limits. The design engineer must accomplish the following:

(1) Determine the actual quality of the makeup water and set water quality limits for the recirculating cooling water.

(2) Measure the softener efficiency and calculate the rate of sidestream flow by mass balance analysis.

(3) Select the feed rate of softening agents plus acid and additives to remove scale in the softener, adjust the cooling water pH, and to control fouling and corrosion in the cooling system.

This design process requires knowledge of both the applicable water chemistry and the many interactions between the various treatments involved. Results obtained during the actual operation of the softener and cooling system may also suggest design improvements as described in this report.

COOLING WATER QUALITY

Cooling water standards define the limiting concentrations of scaling, fouling, and corrosive compounds which contribute to the deterioration of the cooling system (including pipes, filters, and heat exchangers). In sidestream softening, the chromate-base corrosion inhibitors protect heat-exchange equipment and are recycled with the cooling water. Likewise, oxidizing agents used as biocides to control fouling pass through the softener intact. Therefore, the softener design process is primarily concerned with the scaling potential of the cooling water, and removal of scale-forming elements, namely, calcium and silica. Water quality standards are determined by the acidity of the cooling water and the solubility product constants of calcium carbonate. If greater accuracy is required, the solubility product can be corrected to account for the effects of temperature and activity.

Calcium

Calcium forms scale by precipitation as calcium carbonate and/or calcium sulfate. Calcium precipitation is a function of both ion concentration and the pH of the cooling water. Scale formation as calcium carbonate ($CaCO_3$) is shown by the solubility equation:

$$\frac{(Ca^{2+})(CO_3^{2-})}{CaCO_3} = K_{sp}$$

where K_{sp} is the solubility product for calcium carbonate. When the product of the calcium and carbonate free ion concentrations exceeds the solubility product, calcium carbonate will precipitate forming scale. At 25°C, where the activity coefficient is unity, $K_{sp} = 4.82 \times 10^{-9}$ (moles).

However, carbonate ion concentration is also a function of:

$$\frac{[H^+][CO_3^{2-}]}{[HCO_3^-]} = K_2 = 4 \times 10^{-11}$$

The higher the hydrogen ion concentration, the lower is the pH, and the proportion of carbonate ion in the cooling water decreases. In fact, calcium carbonate scale formation is usually prevented by controlling the pH of the cooling water between 6 and 7. Carbonate concentrations are very low in this pH range so that the little calcium carbonate present will remain soluble.

Calcium sulfate is controlled by limiting the concentration of calcium. Klen [1] found in pilot tests that calcium sulfate scale did not form in cooling water with calcium present in concentrations less than 700 mg/L as $CaCO_3$, even when sulfate concentrations exceeded 50,000 mg/L.

Below 42°C, the hydrated form of calcium sulfate is most common ($CaSO_4 \cdot 2H_2O$); at higher temperatures, the anhydride ($CaSO_4$) can be found. Since solubility decreases with temperature, the hottest heat exchanger temperature controls the precipitation reaction.

As a rule, calcium sulfate scale will form when the calcium concentration of cooling water exceeds 280 mg/L. Empirical measurements of calcium sulfate scale formation also indicate that the "cycles of concentration" a given cooling water can undergo without forming precipitate are limited by the solubility product for $CaSO_4$.

Silica

Silica scale occurs in the form of silica dioxide (SiO_2), a polymeric colloid which forms slowly when the silica solubility concentration is exceeded for a given temperature. Determination of the maximum allowable silica concentration is based upon the coldest heat exchanger temperature as follows:

$$SiO_2\ (mg/L) = 4.7T + 24$$

where T is the temperature of the coldest exchanger in °C.

Magnesium silicate or sipiolite ($MgO \cdot 3SiO_2 \cdot 3.5H_2O$) precipitate in the cooling water system if the magnesium concentration in the cooling water is sufficiently high. However, since both magnesium and silica are removed in the softener (i.e., they are not conservative constituents), sipiolite scale need not be considered as a parameter in preliminary softener design.

Other scale-forming compounds include calcium phosphate, iron oxide, and barium sulfate [3]. Calcium phosphate can become a precipitation problem when the makeup water contains sufficient phosphate or if phosphate-based inhibitors are used to control corrosion. High concentrations of phosphate inhibitors interfere with the softening reaction, and should not be used with a sidestream softening system. Makeup water phosphate concentrations are normally quite low (1 ppm). Neither iron nor barium are likely to be present in cooling tower makeup water in concentrations to be included in preliminary design.

SIDESTREAM FLOW RATE

Once the actual makeup water quality has been determined, and the cooling water quality limits have been established, the quality of the softener effluent must be estimated. Softener flowrate can then be based on a mass balance over the entire cooling water system. Calculation of chemical feed rates to completes the preliminary design.

The water quality of a reuse stream will determine its input location. Relatively clean water can be added directly to the cooling tower basin (see Figure 2-1). Reuse streams containing high suspended solids may be input just before the filters in the sidestream treatment train. Other reuse streams can be routed through the softener.

The total sidestream flow may therefore be a blend of plant waste plus a recycle stream. Water quality variations will define a sidestream water composition which should reflect the worst reasonble operating conditions. Recirculating water quality must also be estimated and then checked after sizing the softener flow rate.

Softener Efficiency

The procedure for estimating the efficiency of the softening process is similar to that used to establish water quality standards. It describes the softener reaction in terms of relevant chemical equations and adjusts equations for the effects of temperature and ionic strength. It defines the chemical equations that the remove calcium and silica in the softener.

As reported by Matson and Harris [3], the concentration of calcium remaining in solution in the effluent from a typical softener is much greater than that predicted by the calcium carbonate solubility product constant. The difference may be attributed to kinetic limitations, e.g., a supersaturation of calcium ions in the softener which results in the formation of ion pairs [4]. Based on a typical residual calcium concentration of 30 mg/L as $CaCO_3$ at 20°C, $I = 0.02$, Matson developed an "apparent" solubility product for calcium carbonate formed in the softener:

$$K_{sp(app)} = [Ca^{2+}][CO_3^{2-}] = (30)\times(30) = 900 \text{ mg/L as } CaCO_3$$

where $K_{sp(app)}$ is the apparent solubility product constant.

This apparent constant can be further modified to accommodate variations in temperature [6], such that

$$K_{sp(app,\ T°C)} = K_{sp(app,\ 20°C)} \times \frac{K_{sp}(T°C)}{K_{sp}(20°C)}$$

In addition, the effects of ion activity may be expressed as [7]

$$pK_{sp(app,\ corr)} = \frac{K_{sp(app,\ T°C)}}{\gamma_d^2}$$

where γ_d is the divalent ion activity coefficient for a particular solution, calculated from the Davies equation. The corrected apparent solubility product constant, $K_{sp(app,\ corr)}$ may be assumed to apply to a solution in which the calcium and carbonate concentrations are equal [8]; thus the effluent calcium concentration is defined

$$CaH_{eff} = K_{sp(app,\ corr)}$$

Determination of effluent silica concentration involves additional computation. Silica is removed by adsorption onto magnesium hydroxide floc, which precipitates at high pH. Adsorption is described by the Freundlich equation, in which

$$\frac{SiO_2}{Mg(OH)_2} = k(C_{SiO_2})$$

where $\frac{SiO_2}{Mg(OH)_2}$ = silica adsorbed per mass of hydrogen floc precipitate (mg/mg)

k, n = physical constants derived empirically from silica/magnesium adsorption isotherms

Magnesium concentration in the softener effluent, on the other hand, is calculated by the solubility product constant:

$$(Mg^{2+})(OH^-)^2 = K_{sp} = 10^{-11.6}\ (25°C,\ 1\ atm)$$

The difference between the initial and effluent magnesium concentrations is the magnesium precipitate which enters into the Freundlich equation above. Thus, the effluent magnesium concentration is controlled by adjusting the softener pH which also removes silica.

Final calculation of softener effluent silica concentration for design purposes requires additional mass balance analysis for the cooling system, as follows.

Mass Balance Analysis

The mass balance analysis traces the fate of significant constituents throughout the softening and cooling cycles to determine the necessary softener flow rate and the characteristic concentrations of the recycled cooling water.

The zero discharge sidestream softening system is essentially a closed cooling system. Once materials enter the system, they will remain within the system. They could be removed in the softener, the filters, or by drift loss. the addition of lime, caustic, soda ash, and/or magnesium salts will precipitate calcium carbonate, magnesium hydroxide, and silica. The high pH and alkali in the softener will also precipitate iron, zinc, trivalent chromium, and phosphates.

Most suspended materials are removed, including biological organisms, corrosion residue, and some pretroleum hydrocarbons. If any materials are precipitated, from either added chemicals or reactions within the system, these are removed in the softener and filters.

Some materials entering this system are assimilated. An example is organics reacting with an oxidizing agent such as chlorine. Ammonia and some light hydrocarbons are lost by air-stripping from the recirculating water in the cooling tower. However, nonvolatile materials that remain soluble will pass through the softener and filters to recycle within the system. These are chlorides, sulfates, hexavalent chromates, bromides, and molybdates.

In zero blowdown systems, (Figure 2-1), the concentrations of these ions are controlled by drift losses, such that (at steady state)

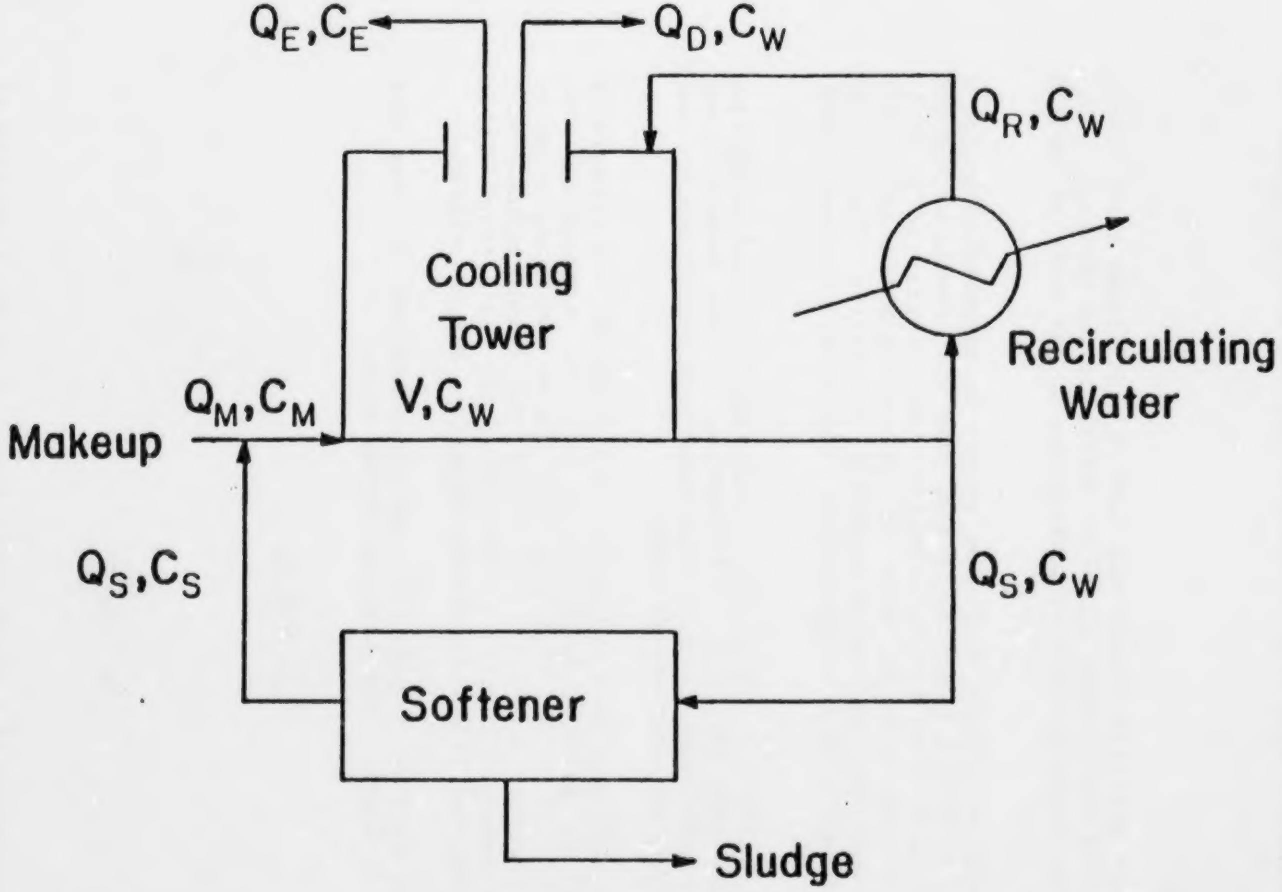
$$C_m Q_m = C_w Q_d$$

or

$$C_w = C_m \left[\frac{Q_m}{Q_d} \right]$$

where C is the concentration of a given constituent, Q is the flow rate of water in the system, and the subscripts m, w, and d indicate the location of concentration and flow as that of the makeup water, cooling water, and drift, respectively. (The drift rate, Q_d, is often approximated on the basis of cooling water evaporation rate).

The nonconservative dissolved solids removed in the softener are cal-


Q_E, C_E
Q_D, C_W
Q_R, C_W
Cooling Tower
V, C_W
Recirculating Water
Makeup
Q_M, C_M
Q_S, C_S
Q_S, C_W
Softener
Sludge

Schematic Diagram Of Sidestream Softening System

Figure 2-1.

cium, magnesium, carbonate, and silica. A mass balance over the cooling tower is expressed by the steady state expression

$$Q_m C_m + Q_s C_s = Q_d C_w + Q_s C_w$$

where Q_s and C_s are the flow rate and constituent concentration going into the softener loop.

The softener sidestream flow rate, Q_s, is determined by the relative concentrations of the controlling constituent.

$$Q_s = \frac{Q_m C_m - Q_d C_w}{C_w - C_s}$$

Q_m is determined by heat dissipation requirements, C_m is determined by analysis of the raw water source. C_w is defined according to the previous section on cooling water quality. The only unknown on the right-hand side of this mass balance equation is C_s. While C_s for calcium is calculated as softener efficiency, determination of the silica concentration of the softener effluent requires several additional steps to compute. When the above equation is solved for the cooling water constituent concentration, C_w, and the expression for C_w is substituted into the Freundlich equacion for silica adsorption, the Q_s term cancels out and the resultant equation yields

$$C_{s(Si)}^{\;1/n} = \frac{1}{k}\left[\frac{Q_m C_{m(Si)} - Q_d C_{s(Si)}}{Q_m C_{m(Mg)} - Q_d\, k_{sp}(H^+/k_w)^2}\right]$$

This equation may be solved for C_s to yield the softener effluent silica concentration and can be used to solve for Q_s as described. Since calcium and silica determine two independent sidestream flow rate values, the larger value for the sidestream flow rate, Q_s is necessary to attain the required cooling water quality, and the determining constituent is said to control.

Complications arise if insufficient magnesium is present in the makeup water to adsorb the silica. The solution to the above equation will, therefore, yield a $C_{s(Si)}$ greater than the upper limit even if the pH is high. An external source of magnesium must then be added.

SOFTENING AGENTS, pH ADJUSTMENT AND ADDITIONAL TREATMENT

Once the softener flow rate has been selected, the rate of addition of softening agents (either lime or caustic) can be easily calculated according to the stoichiometric equivalents of the scale-forming elements removed. Subsequent acidification (H_2SO_4 or CO_2) regulates the pH of the softener effluent and the recirculating cooling water in order to prevent precipitation of calicum carbonate in the cooling system. Additional treatment may be required to prevent corrosion or fouling.

Softening Agents

Lime or caustic are added to raise the pH of the softener to the point where calcium and magnesium will precipitate as calcium carbonate and magnesium hydroxide. Since bicarbonate converts to carbonate at pH higher than 10.4, and the pK_{sp} of magnesium hydroxide is 10.7, the pH of the softner is generally raised to between 10.5 and 11.0, depending on temperature. Addition of lime or caustic is determined by the amount required to 1) neutralize the alkalinity of the cooling water sidestream and convert it to the carbonate form; 2) raise the softener pH to the proper level; and 3) precipitate the magnesium as $Mg(OH)_2$. This calculation is usually accomplished by expressing all constituents in terms of parts per million of calcium carbonate equivalents (ppm $CaCO_3$), such that

$$[\text{CaOH, NaOH}] = [\text{Alkalinity}] + [Mg^{2+}] + [OH]_{\text{final}}$$

Also note that when alkalinity is measured at the methyl orange titration point (4.5), the corresponding lime required must be doubled to insure conversion of all the alkalinity to the carbonate form.

When lime is used for pH adjustment of the softener water, in some cases, soda ash may be required to provide enough carbonate for complete calcium precipitation. Soda ash requirements are calculated as the difference between calcium and alkalinity in the pH adjusted softener water; hence

$$[Na_2CO_3] = [Ca^{2+}] + [Ca^{2+}]_{\text{added}} - 2[\text{Alkalinity}]$$

The alkalinity concentration (in ppm $CaCo_3$) is usually doubled to account for the conversion of monovalent bicarbonate to divalent carbonate.

pH Adjustment

Calcium carbonate scale is controlled by pH of the cooling water within the limits of $CaCO_3$ saturation, usually in the range of pH 6 - 8. The pH may be lowered by addition of sulfuric acid, or by carbon dioxide. Sulfuric acid increases the TDS by adding sulfates to the cooling water. Carbon dioxide is air-stripped in the cooling tower so that excess carbon dioxide must be replinished. Furthermore, carbon dioxide cannot reduce alkalinity, so that in certain circumstances, acid addition is preferred.

Some cooling water system are being operated at the higher range of pH 7 - 8.5. The advantages for a sidestream-softened system are (1) less lime or caustic is required to raise the pH of the softener sidestream; (2) less acid is reuired to lower the pH of the softener effluent; and (3) reduced TDS results in reduced corrosion potential. However, when cooling water acidity is maintained so close to the pH of calcium carbonate saturation (pH_s), careful monitoring is necessary to prevent the accidental formation of scale.

When calculating the pH_s of the cooling water, allowance must be made for the effects of ionic strength and ion pairing. According to McGaughey and Matson [9], when the formation of calcium sulfate ion pairs ($CaSO_4^0$) are taken into account, saturation pH can be equated such that

$$pH_s = pK_2 - pK_{sp} - \log T_{Ca} - \log Alk - \log \frac{\gamma_1^5}{1 + K_a \gamma_1^8 T_{SO_4}}$$

where k_2 = second acidity constant for carbonate system

K_{sp} = solubility product constant for calcium carbonate

T_{Ca} = total calcium, m/L

T_{SO_4} = total sulfate, m/L

Alk = total alkalinity, m/L

γ_1 = activity coefficient (from Davies equation)

The saturation pH determined by the McGaughey method is higher than would be without correcting for ion pairs.

Acid feed rate is calculated from stoichiometric equivalents required to neutralize alkalinity and lower the pH to the predeterminied pH_s. Acid addition is in the softened sidestream, and in the cooling tower basin. Sulfuric acid dosage need be equal to the total alkalinity of the makeup water and the softener effluent sidestream, plus the stoichiometric equivalents required to lower the pH of the effluent to the saturation pH,

$$[H_2SO_4] = [TAlk]_m + [TAlk]_s + \log^{-1} (pH_s)$$

While sulfuric acid is most commonly added to acidify the softener sidestream, carbon dioxide has been suggested as an alternative, and is currently being used for pH adjustment at the USS Chemicals sidestream softening system. Perhaps the main advantage to carbon dioxide as an alternative to sulfuric aci is that it does not increase the level of sulfates in the cooling water. Lower sulfate levels decrease the corrosivity of the cooling water, as well as the TDS. Also, the dangers of acid overdose are minimized with carbon dioxide since, unlike sulfuric acid, an excess of CO_2 will never drop the pH of the cooling water below 4.3 (i.e., the pH at which CO_2 is no longer absorbed). Acidification with carbon dioxide maintains the alkalinity of the cooling water and reduces the soda ash requirements. Since high alkalinity can also increase calcium carbonate precipitation, one can add some sulfuric acid to the softener sidesream effluent. This destroys residual alkainity and precipitates ionic silica. In practice, carbon dioxide can be added to the cooling tower basin to lower the pH of the cooling water before it reaches the heat exchangers.

Additional Treatment

Compounds are added to cooling water to control scaling, corrosion, fouling, and microbial growth. Many of these substances interfere with the softening reaction and cannot be used in a zero-discharge system. Each additive must be evaluated individually to its compatibility with the sidestream softening process.

Scale inhibitors, such as phosphate esters, phosphonates, and polyacrylates, are very effective even at relatively low dosages. They keep scaling minerals in solution even in water with high scaling potential. They also prevent precipitation in the softener. Their effect must be offset by the addition of excess lime or caustic that results in higher effluent calcium hardness. The same may be said of lignins, tannins, alginates, and starches, all of which have been used to reduce scale. A recent development in scale prevention involving modification of the scale crystal structure has been found to have no deleterious effect on softener efficiency. It even produces a better quality softener effluent when soda ash is used to supply alkalinity. Most scale inhibitors are removed in the softener and need to be added continuously.

Corrosion control is often achieved by the addition of chromate-base corrosion inhibitors. Hexavalent chrome is not removed in the softener. It is recycled to the cooling tower system, as are concentrations of other conservative ions (such as chloride and sulfate) that require higher levels of corrosion inhibitor. Chromate levels in several systems have been increased from 20 to 50 ppm to prevent pitting on the heat exchangers. Nonchromate inhibitors include phosphates, polyphosphates, molybdates, silicates, and nitrates. The polyphosphates cause "after-precipitation," and are removed in the softener along with the silicates when sufficient magnesium is present. Other phosphates, including orthophosphate, are removed in the softener, but do not interfere with softener efficiency. Trivalent chromium, precipitates out in the softener and is removed as a sludge.

Suspended solids or foulants from any number of sources are controlled by the addition of dispersants or suspending agents (including polyacrylates). Generally, they are all incompatible with the operation of the sidestream softener. They prevent the softener sludge from settling. The nonionic low-foaming surfactants used to control organic foulants (e.g., biological slime). They can disrupt the clarifier bed when they are added on a slug basis. Some of these products are less disruptive than others so one that causes minimal interference should be selected.

It is necessary before selecting a biocide for control of microbiological growth, to determine the fate of the toxicant (1) at the high pH of the softener, and (2) at the high concentration of organic potentially present in the recirculating cooling water. Where the cooling system pH varies from approximately 8 to 11, the biocides will increase in concentration, either as added or in some degraded form. For example, chlorine is reduced to chloride and increases the corrosivity of the recirculating water. Also, it is ineffective at high alkalinity. By comparison, chlorine dioxide has fewer chlorides and still retains its effectiveness in the softener. The hypochlorite ion will pass through the softener if the chlorine demand of the $CaCO_3$ slurry is low. Other oxidizing biocides (bromine, ozone, H_2O_2) also control microorganisms at relatively high pH without forming dissolved solids. Nonoxidizing agents which contain dispersants are not suited for sidestream softening for the reasons given above.

SECTION 2 - REFERENCES

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SECTION 3

SIDESTREAM SOFTENER OPERATION AT USS CHEMICALS

The USS Chemicals plant was construction in 1961 on a 60-acre plot in Pasadena, Texas near Houston. The plant manufactures basic chemical feedstocks, ethylene and styrene). Capacity for the ethylene unit is 500 million pounds per year and for the styrene unit, 120 million pounds per year.

In November 1979, the plant was converted to a minimum aqueous discharge system with sidestream softening (Figure 3-1). A flow diagram for the water recycle system is given in Figure 3.2. The plant has two cooling towers. They operate at 110 to 170 cycles of concentration. A sidestream of hot cooling water is pumped from each tower to a splitter box, which feeds the lime softeners. Two softeners (referred to as "North" and "South") in parallel remove high concentrations of calcium, magnesiim, and silica from the cooling water. Lime is added as a slurry to raise the pH in the softener above 10, and soda ash (Na_2CO_3) is added to provide sufficient carbonate to complete the softening reaction.

After softening, the sidestream is acidified by injection of carbon dioxide (CO_2) in the recarbonator. The softened water is then filtered to remove any small particulate matter which did not settle in the softener or recarbonator units, and returned to the cooling tower.

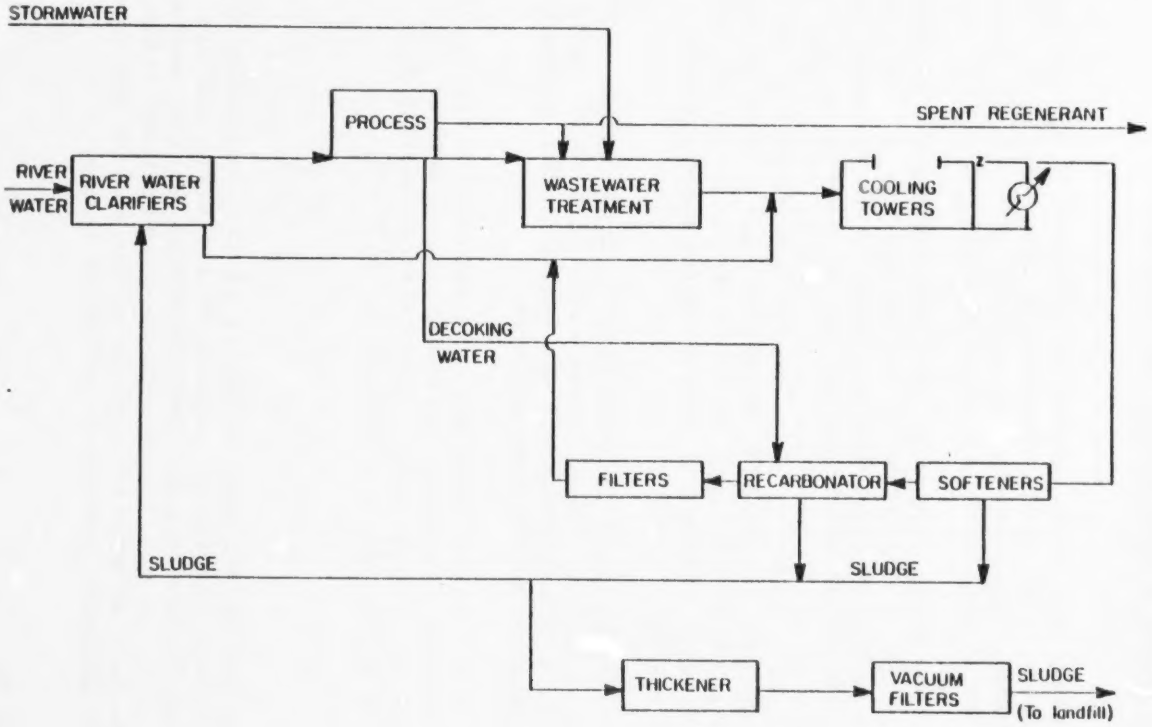
The USS Chemicals water reuse system also incorporates other recycle streams, some of which contain processed wastewater, characterized by high TDS, TSS, and organic and oil contaminants. Average water quality data for the USS Chemicals softener sidestream is presented in Table 3-1.

OPERATIONAL DATA

Since the start-up, the sidestream softening at USS Chemicals, much effort has been inputted into careful monitoring of the water quality. A sizeable record of information has been obtained concerning chemical consumption rates, corrosion rates, and quality of both makeup water and softener effluent. Together, they form an accurate profile of the startup and operation of a successful zero discharge sidestream softening system.

Hardness, Alkalinity, and pH

Among all water quality parameters, the most critical to the sidestream softener operation are calcium hardness (CaH), total alkalinity (T-Alk), and


STORMWATER
PROCESS
SPENT REGENERANT
RIVER WATER
RIVER WATER CLARIFIERS
WASTEWATER TREATMENT
COOLING TOWERS
DECOKING WATER
FILTERS
RECARBONATOR
SOFTENERS
SLUDGE
SLUDGE
THICKENER
VACUUM FILTERS
SLUDGE
(To landfill)

USS CHEMICALS PROCESS FLOW SCHEMATIC OF THE MAXIMUM RECYCLE, SIDESTREAM SOFTENING SYSTEM

Figure 3-1. Schematic diagram of USS Chemicals sidestream softening system.

FLOW DIAGRAM FOR WATER RECYCLE SYSTEM

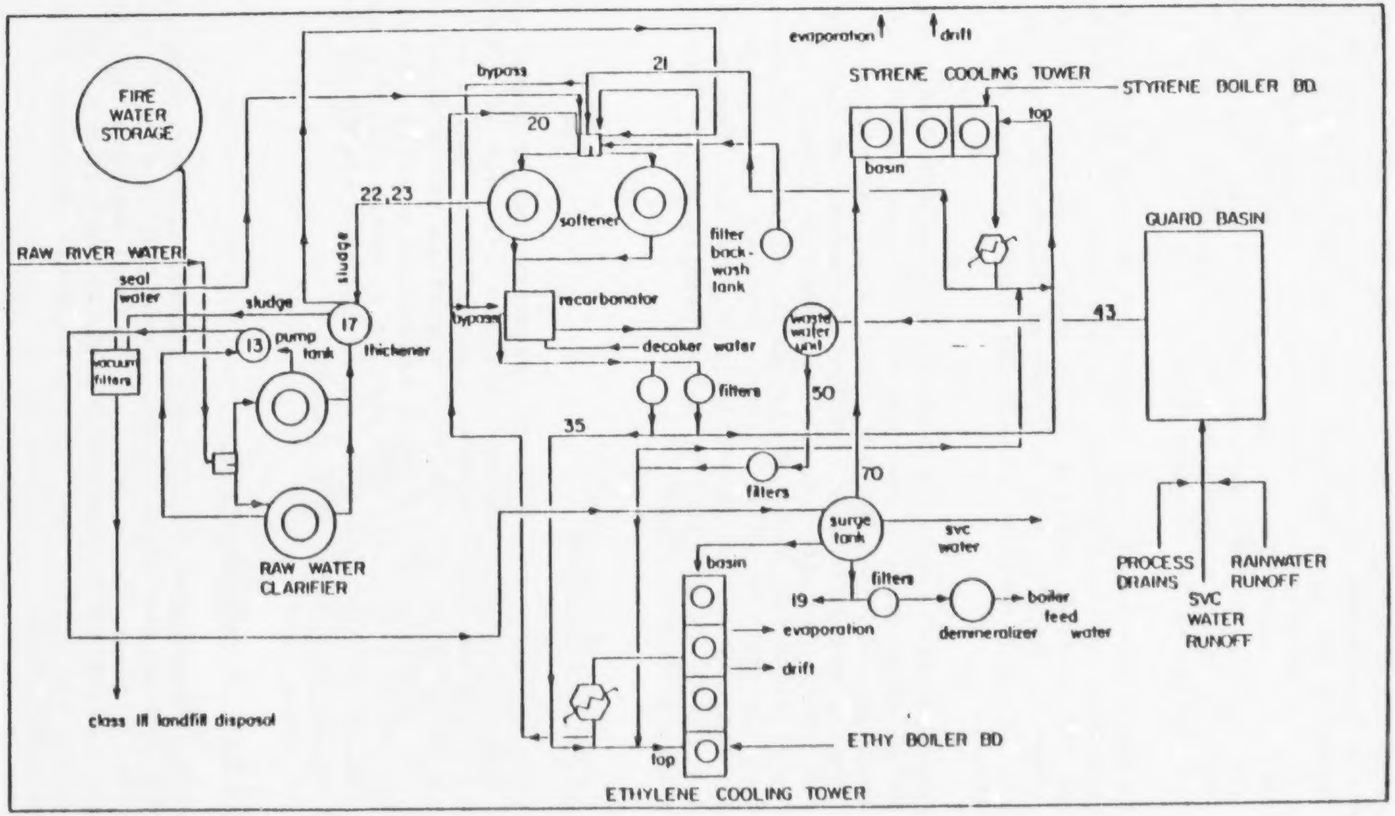

evaporation
drift
STYRENE COOLING TOWER
STYRENE BOILER BD
top
basin
bypass
21
20
FIRE WATER STORAGE
22,23
softener
filter back-wash tank
GUARD BASIN
RAW RIVER WATER
seal water
sludge
sludge
17
13
pump tank
thickener
vacuum filters
recarbonator
bypass
decoker water
waste water unit
43
filters
50
35
filters
70
surge tank
svc water
RAW WATER CLARIFIER
basin
filters
19
boiler feed water
demineralizer
evaporation
drift
PROCESS DRAINS
SVC WATER RUNOFF
RAINWATER RUNOFF
class III landfill disposal
ETHY BOILER BD
top
ETHYLENE COOLING TOWER

Figure 3-2.

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pH. Data for these variables collected from five separate sampling points are presented in Figures 3-3 through 3-11. Since both the north and south softeners received the same influent, the similarity of their effluent quality (Figures 3-3 through 3-5) was expected. Furthermore, variations in softener effluent quality can be seen to error, roughly, the quality of the influent from the ethylene and styrene cooling towers (Figures 3-6 through 3-8). Water quality in the recarbonator shows the effect of acidification with carbon dioxide (Figures 3-9 through 3-11).

The relation between calcium removal and softener pH can also be derived from a comparison of Figures 3-3, 3-7, and 3-10. The difference between influent CaH and calcium hardness in the recarbonator (i.e., calcium removed) does not appear to increase with softener pH, suggesting that the addition of more lime to increase softener pH does not serve to improve calcium removal in the softener.

A "trend analysis" performed over the eight-month period from September 1, 1980 through April 30, 1981 revealed no continuous trends, either increasing or decreasing. The pH, CaH, and T-Alk variables are presented appropriately in terms of mean (average), standard deviation, and confidence interval in Table 3-2. Data for both tabular and graphical formats were obtained by plant operators every two hours at the north and south softeners, and every four hours at the other sampling points. The data was averaged over ten-day periods, as indicated on the time-axis of Figures 3-3 through 3-11; for the purpose of trend analysis, data were analyzed by 21-day "moving" averages over the entire 242-day period.

Magnesium Hardness and Silica

Softener influent and effluent concentrations of magnesium and silica were also monitored concurrently. Figures 3-12 and 3-13 present water quality data for these from February to April, 1981. Silica concentration in the softener effluent is a function of magnesium in the softener influent. Therefore, an increase in influent magnesium usually corresponds to a decrease in effluent silica. Alternatively, where influent magnesium is constant, changes in the levels of silica in the softener effluent parallel changes in silica in the softener influent.

Water quality and Quality Assurance

Comprehensive analyses of different streams in the cooling water recycle system where done on four separate occasions. The average of these analyses was presented earlier (Table 3-1). Individual analyses are presented in tabular form in Appendix B, along with ionic balance sheets. The accuracy of these analyses was established on two separate occasions by independent quality assurance tests.

Split samples were collected on February 17, 1981 from eight streams and four sludge locations, one for the University of Houston laboratory and one for the Robert S. Kerr Environmental Research Laboratory (EPA) in Ada, Okla-

TABLE 3-1. Average Water System Sample Analysis*

Location	No.	Ca^{2+}†	Mg^{2+}†	K^+	Na^+	Cl^-	T.Alk†	SiO_2	pH	TDS	Turbidity (NTU)	TSS	TOC
Treated Raw Water	13	108	15	14	35	46	76	7	7.74	210	2.5	85.5	7
Ethylene Influent to Softener	20	276	30	343	9,195	11,100	391	62	7.40	26,000	42.8	256	548
Styrene Influent to Softener	21	282	35	180	5,975	6,444	286	45	7.52	13,700	12.0	141	328
Combined Filter Effluents	35	110	9	434	7,750	8,442	259	46	8.32	24,200	21.1	182.5	476
Guard Basin Effluent	43	126	15	135	2,887	2,971	187.3	23	8.90	5,140	44.4	143.0	214
WWTU Effluent	50	72	8	41	7,075	1,099	90	11	7.51	3,620	41.6	91.5	121
M-1008	70	108	15	14	34	45	76.5	8	7.5	354	6.0	85	8

*All values in mg/L unless otherwise noted

†Values in mg/L $CaCO_3$

TABLE 3-2. COOLING AND SOFTENING SYSTEM AVERAGES SEPTEMBER 1980 THROUGH APRIL 1981

	Calcium Hardness (ppm $CaCO_3$)			Alkalinity (ppm $CaCO_3$)			pH		
	Mean	Standard Deviation	Confidence Interval	Mean	Standard Deviation	Confidence Interval	Mean	Standard Deviation	Confidence Interval
Ethylene Cooling Tower	250.5	47.9	247.4 - 253.7	362.1	99.7	355.5 - 368.8	7.46	7.28 - 7.77	7.44 - 7.47
Styrene Cooling Tower	268.5	33.2	266.3 - 270.6	262.0	67.9	257.7 - 266.4	7.39	7.21 - 7.72	7.38 - 7.41
North Softener	120.8	44.3	118.9 - 122.7	109.7	31.2	108.1 - 111.2	10.25	10.02 - 10.76	10.24 - 10.27
South Softener	120.2	52.9	117.7 - 122.8	111.8	23.6	110.7 - 112.9	10.23	9.97 - 10.93	10.21 - 10.24
Recarbonator	101.6	31.2	99.5 - 103.6	216.7	41.6	214.0 - 219.4	8.21	7.97	8.17 - 9.26

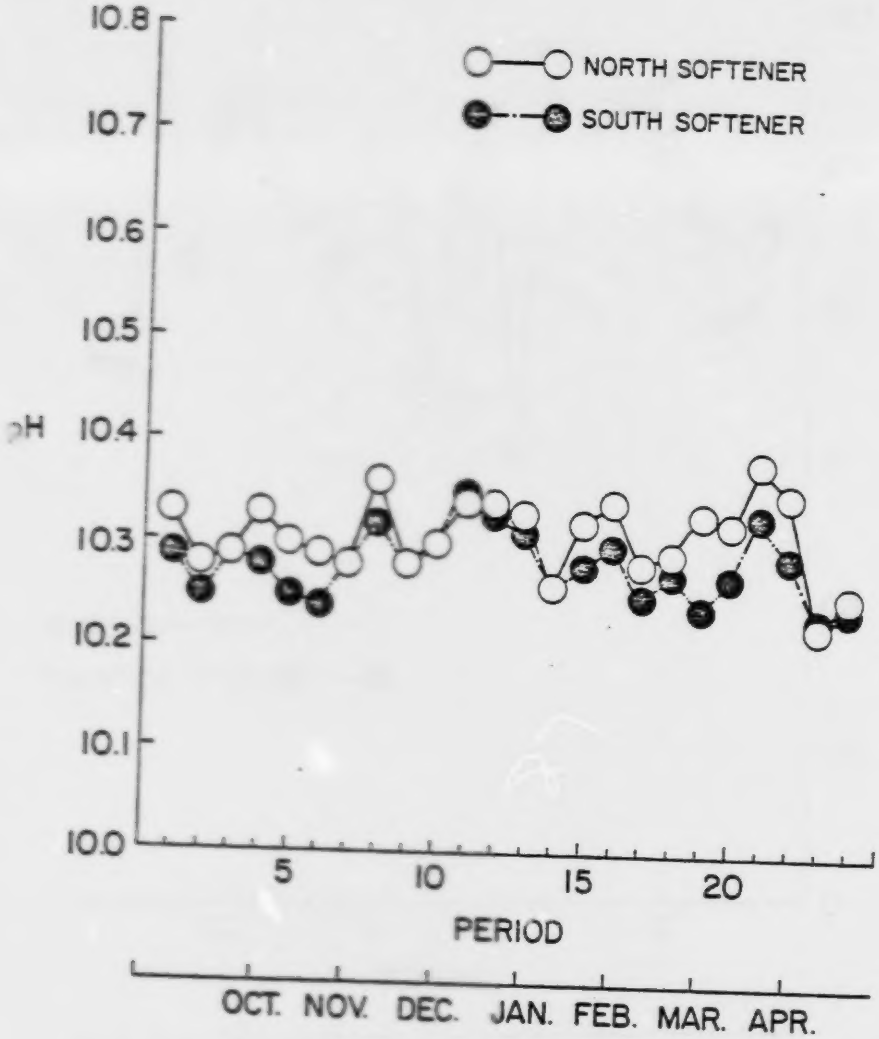


Figure 3-3. Softener effluent pH at USS Chemicals, 1980-81.

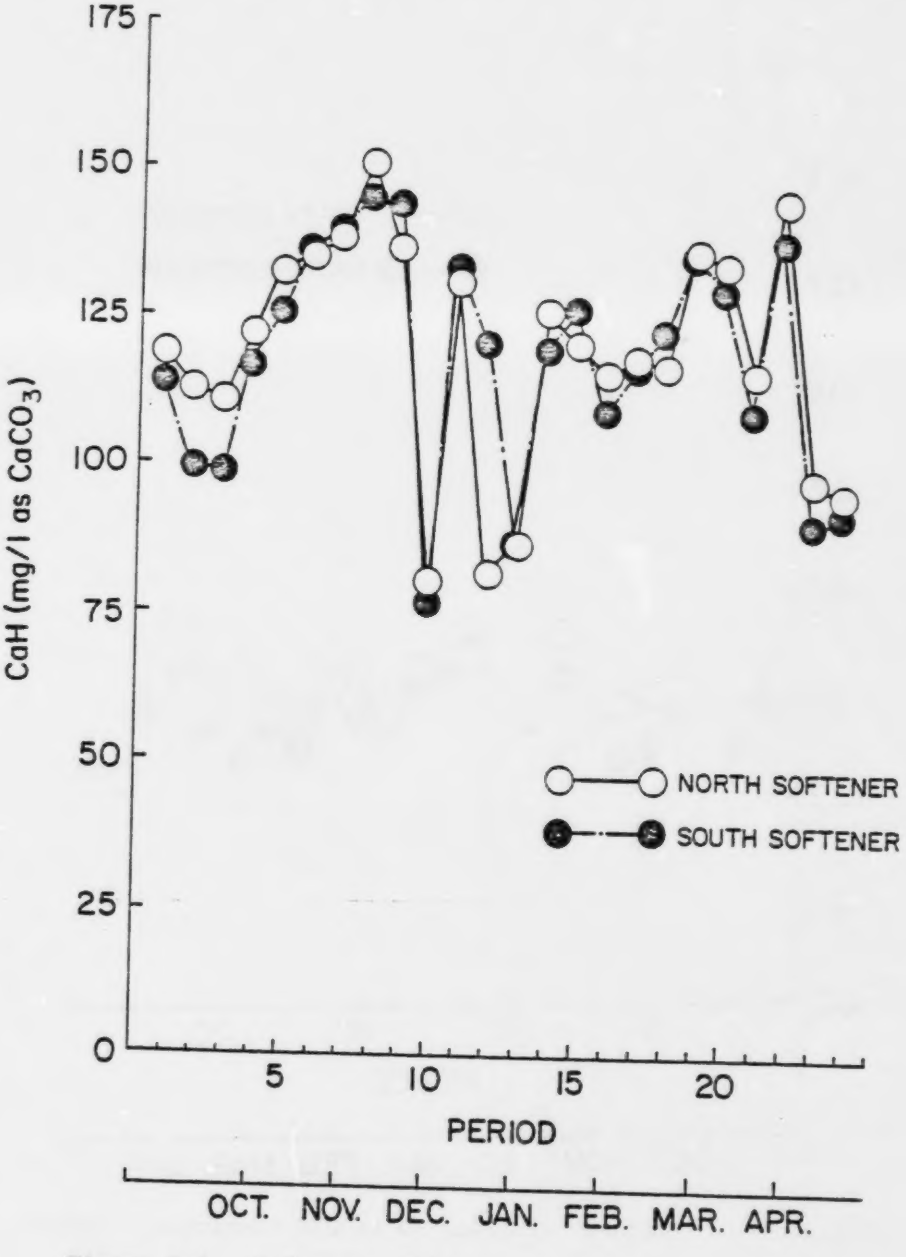


Figure 3-4. Softener effluent calcium hardness, 1980-81.

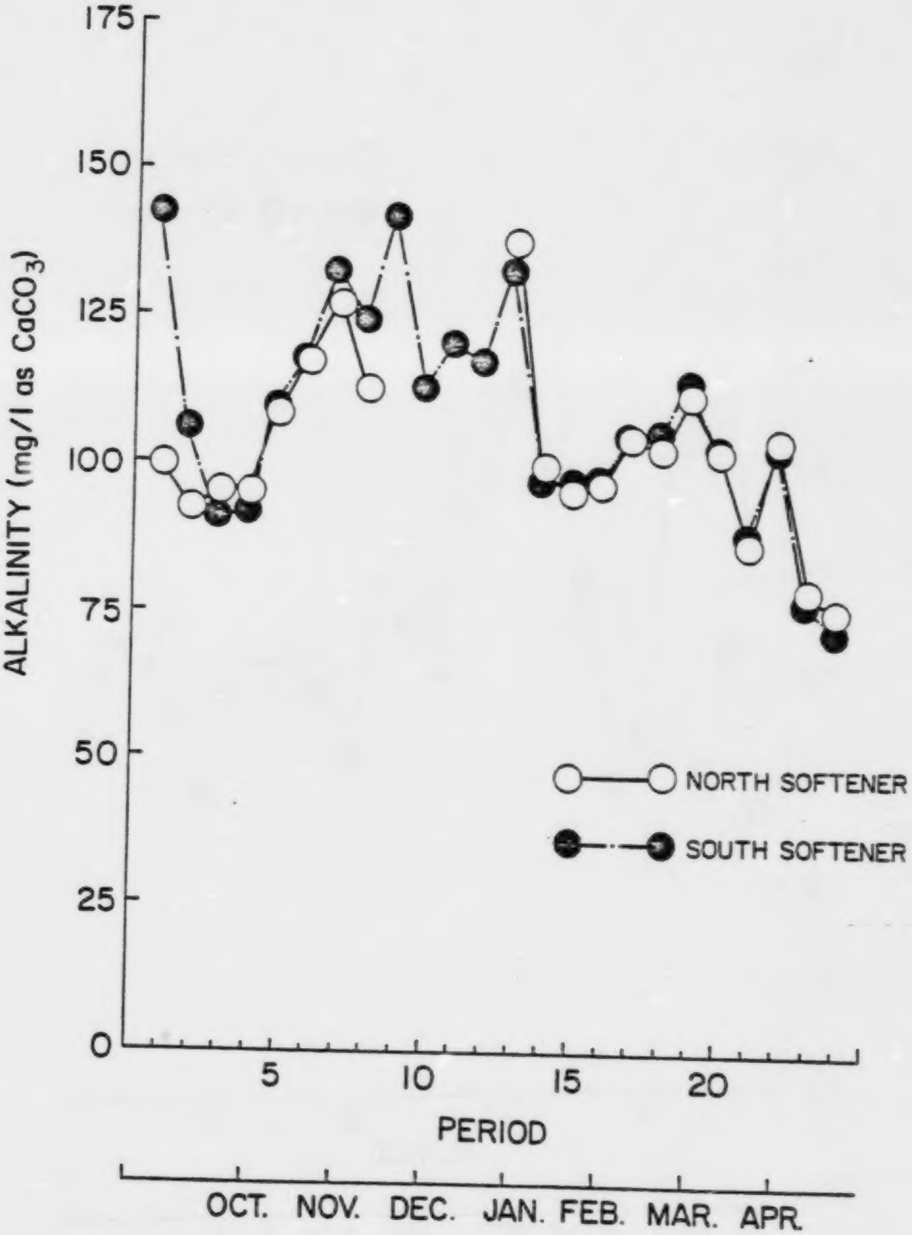


Figure 3-5. Softener effluent alkalinity, 1980-81.

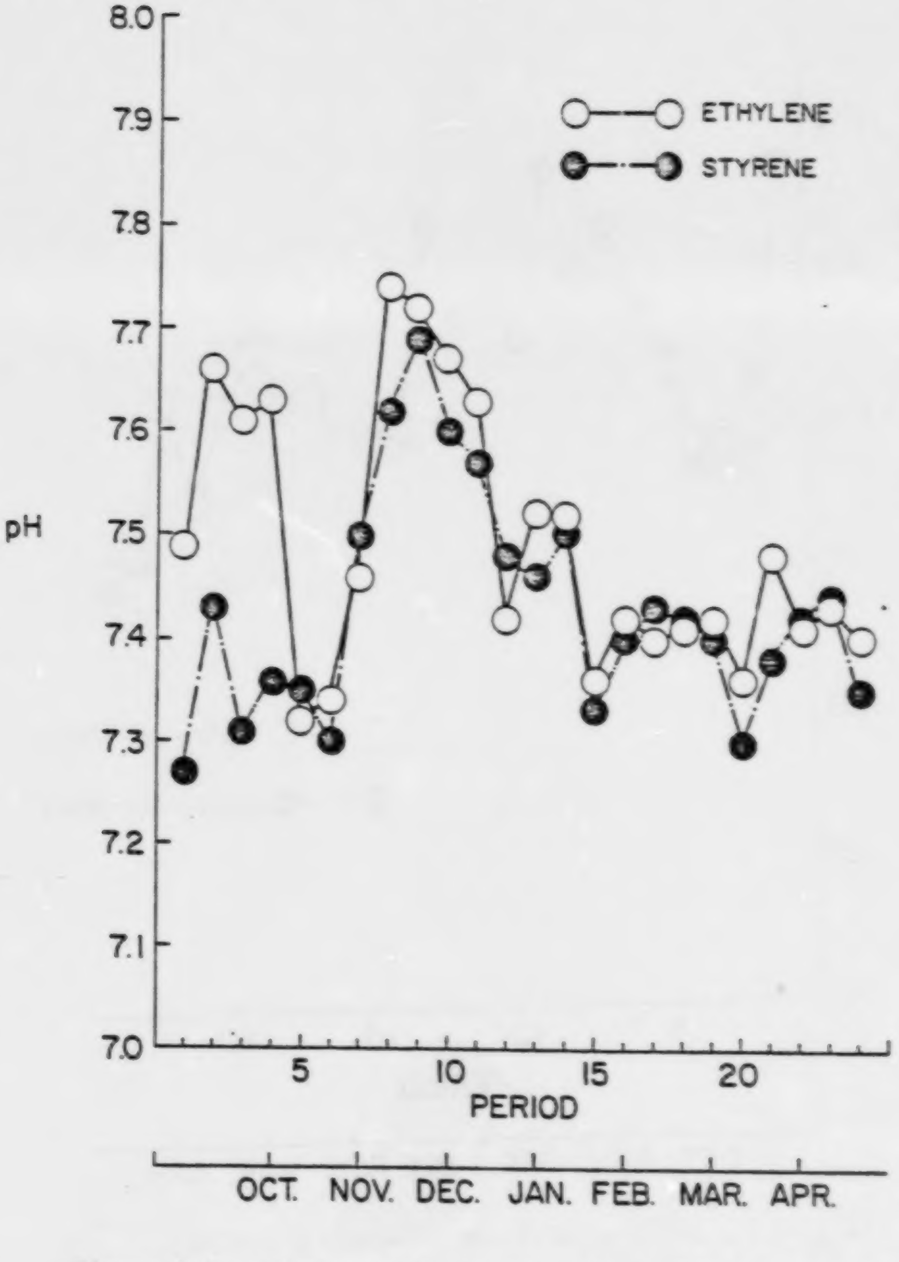


Figure 3-6. Ethylene and styrene unit cooling water pH, 1980-81.

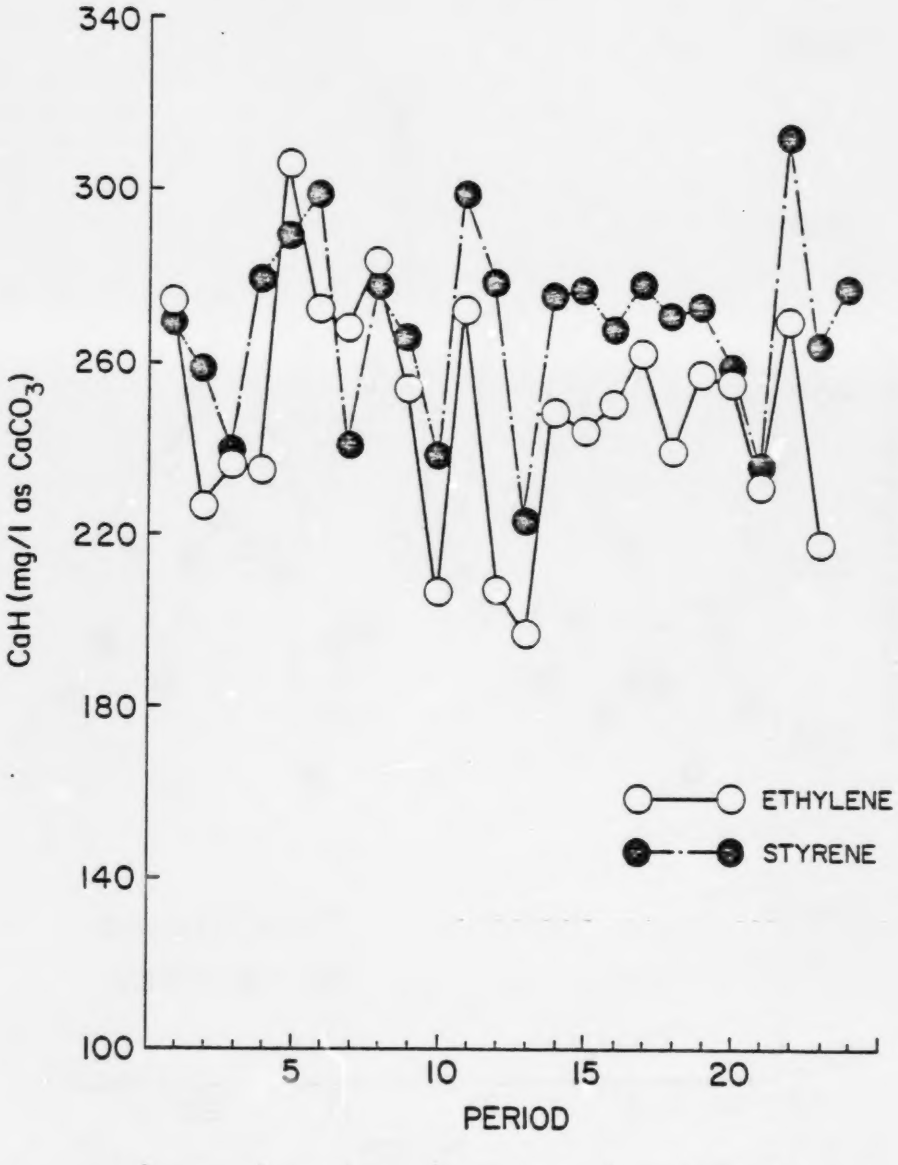


Figure 3-7. Ethylene and styrene unit cooling water calcium hardness, 1980-81.

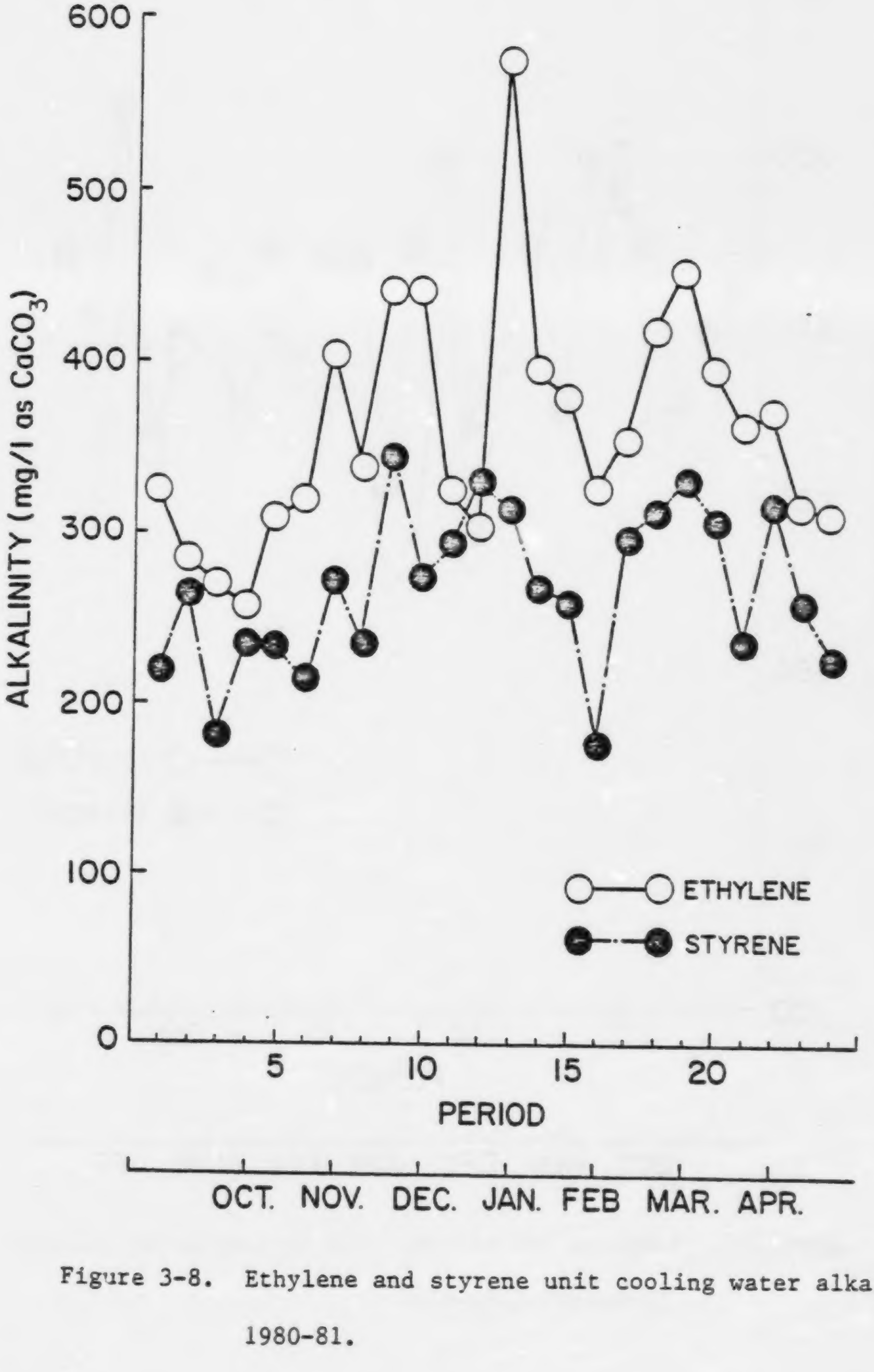


Figure 3-8. Ethylene and styrene unit cooling water alkalinity, 1980-81.

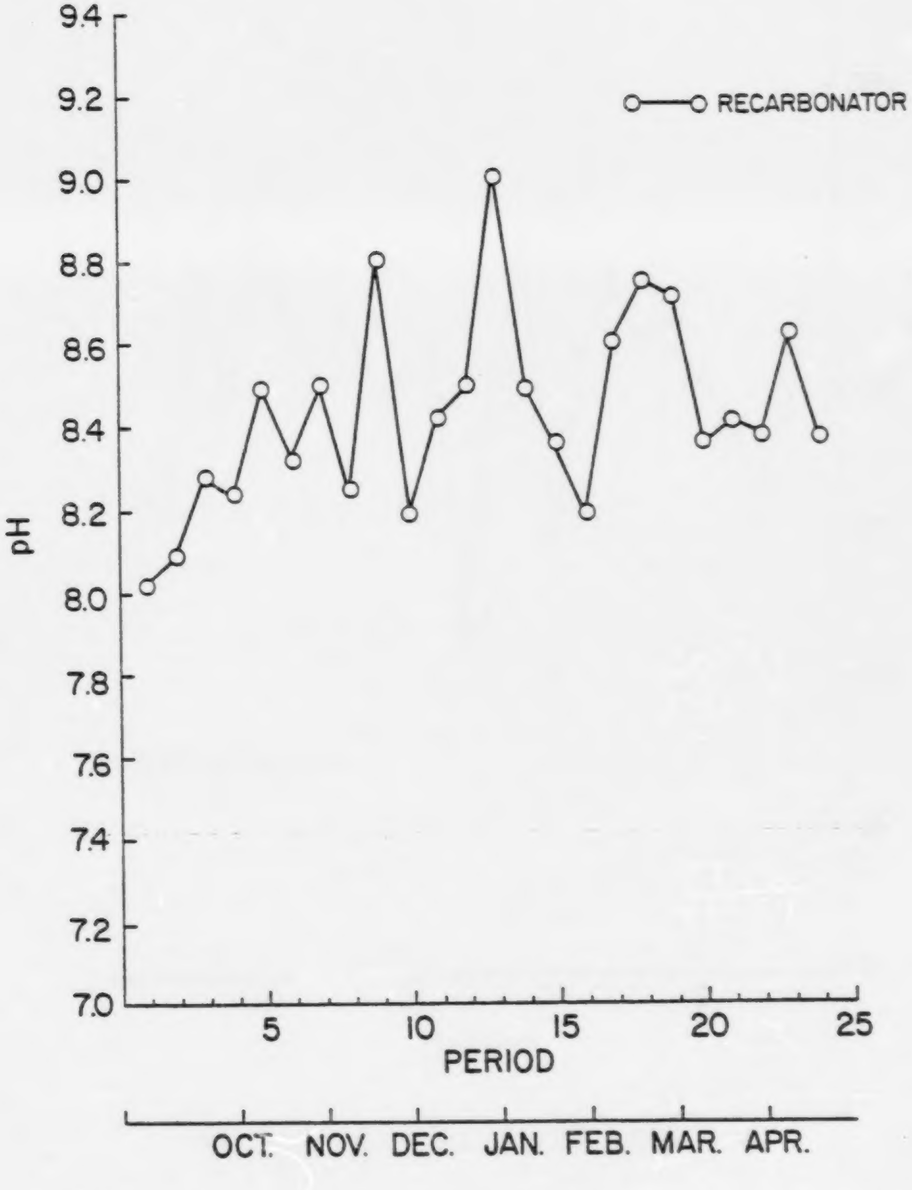


Figure 3-9. Recarbonator pH, 1980-81.

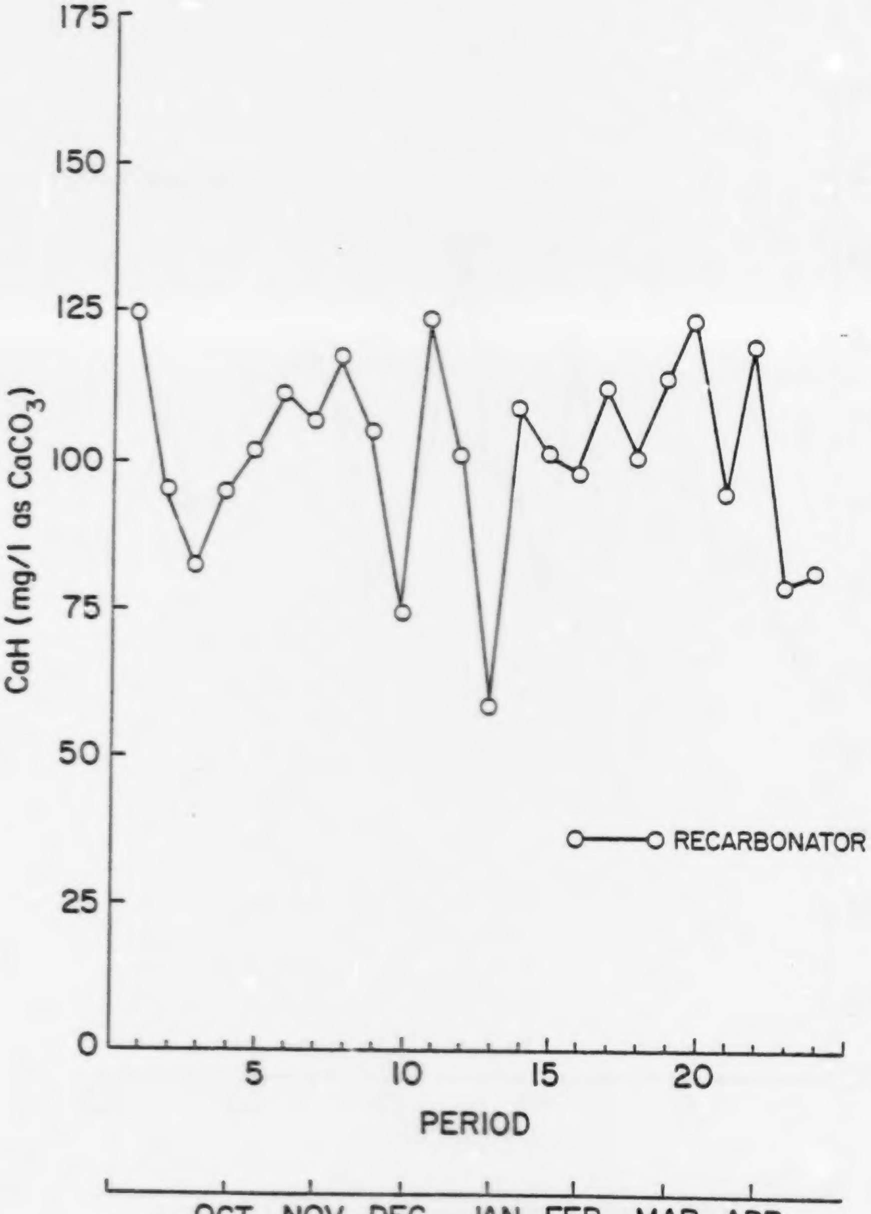


Figure 3-10. Recarbonator calcium hardness, 1980-81.

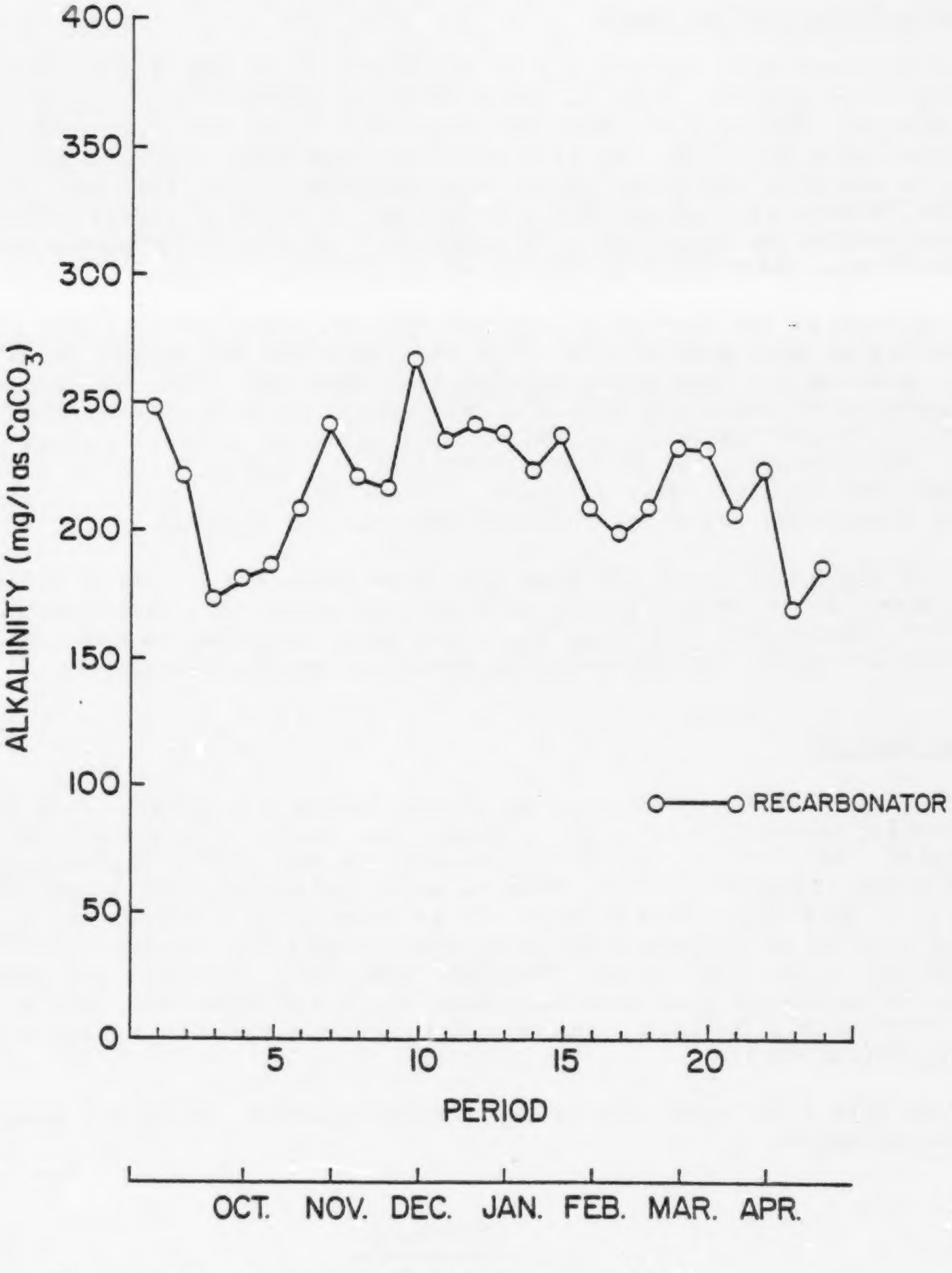


Figure 3-11. Recarbonator alkalinity, 1980-81.

homa. The only difference in the two laboratory analyses was in the measurement of alkalinity. An interference of $CaCO_3$ fines before filtration caused an error in the total alkalinity measured. A quality assurance test was performed by the Water and Wastewater Analysts Association.

Chemical Usage and Cost Rates

Concurrent with the analysis of water quality in the lime softening and cooling water systems, chemical usage rates and chemical costs (cost per day and cost per 1000 gallons) were also monitored. For two periods--from June through September, 1980, and from March through May, 1981--the four costs basic to the lime softening system were measured. Lime, soda ash, CO_2, and sludge for both periods are shown in Tables 3-3 and 3-4. These parameters were calculated by comparing measurements of amounts of chemicals used (or disposed) with usage rates as determined by inventory check.

As regards the lime softening system, the lime calculations for the second period were more precise since only then was the amount of dilution water added to the lime slurry storage tank measured. Also, since most CO_2 consumption occurs in the ethylene and styrene cooling towers, the design rate of 1000 lbs/day to the recarbonator is assumed as the CO_2 consumption rate. (Consequently, the consumption rate of the cooling water is decreased by 1000 lbs CO_2/day.) Best estimates divided the production of filter cake evenly between the raw water clarifier and the lime softener.

Cooling water costs and chemical usage rates are listed in Table 3-6. Since most of the cooling water chemicals are added on a batch basis, consumption figures are usually derived from daily operator records. However, chlorine and carbon dioxide were also monitored by pressure gauges.

Carbon Dioxide

One major disadvantage in using carbon dioxide for control of pH is that the cooling tower acts as a gas stripper that continually removes CO_2 from the water. As a result, carbon dioxide must be continually replenished, and roughly ten times as much CO_2 must be used, as compared to equivalent pH control with H_2SO_4. Furthermore, it is frequently difficult to measure carbon dioxide in cooling water accurately, since CO_2 is often lost to the atmosphere during sampling and transfer. Therefore, a method was developed at the University of Houston to determine CO_2 in USS Chemicals cooling water as a function of alkalinity, and to calculate the extent of CO_2 stripped out by the cooling tower.

The method is based upon an equilibrium equation for carbon dioxide in an aqueous system,

$$K_1 = \frac{(H^+)\ (HCO_3^-)}{(H_2CO_3^*)}$$

TABLE 3-3. Chemical Usage Rates - Lime Softening System

		Sludge*		Lime		Soda Ash		CO_2+	
Dates	# days	#	#/day	tons	lb/day	#	#/day	#	#/day
6/16 - 7/4	20	166,972	8348.6	50.92	5092	11,350	568	20,000	1,000
7/5 - 7/30	26	130,606	5023.3	37.476	2883	20,350	783	26,000	1,000
7/31 - 8/18	19	64,021	3369.5	34.540	3636	16,100	847	19,000	1,000
8/19 - 9/7	19	115,656	6087.2	34.998	3368	21,950	1155	19,000	1,000
9/8 - 9/27	20	127,515	6375.8	32.171	3217	19,000	950	20,000	1,000

*Based upon sludge produced from lime softeners

+Based upon CO_2 added to recarbonator

TABLE 3-6. CHEMICAL USAGE RATES FOR LIME SOFTENING SYSTEM

Dates (1981)	No. Days	Lime		Soda Ash		CO_2*		Filter Cake+ (produced)	
		Dry Tons	Tons/Day	lbs	lbs/day	lbs	lbs/day	lbs	lbs/day
3/5-3/25	21	43.971	2.094	7,700	366.67	21,000	1,000	146,260	6964.8
3/26-4/15	21	40.667	1.937	15,600	742.86	21,000	1,000	104,389	4970.9
4/16-5/6	21	49.765	2.370	19,750	940.48	21,000	1,000	178,560	8502.9
5/7-5/27	21	42.677	2.032	16,300	776.19	21,000	1,000	121,850	5802.4
	Σ wt.	177.080		59,350		84,000		551,059	
	Ave. wt/day		2.108		706.55		1,000		6560.2

* Estimate of dosage to recarbonator

+ Estimate of lime softener sludge produced

TABLE 3-5. Average Chemical Costs and Usage Rates—Softener

	Flow	Lime		Soda Ash		CO_2		Sludge		Total
Period	1000 gal/day	\$/#	#/day	\$/#	#/day	\$/#	#/day	\$/T	T/day	\$/1000 gal
6/16/80 - 9/27/80	871.1	.035	3639.2	.102	860.6	.019	1000	41.03	2.92	.402
3/5/81 - 5/27/81	801.4	.039	4216	.108	706.6	.026	1000	9.88	3.28	.377

TABLE 3-6. Average Chemical Costs and Usage—Cooling Tower

Chemical	$/#	#/day	$/kgal
Calcium Dispersant	1.63	111.5	.041
Zinc Inhibitor	0.67	53.9	.008
Chromate Inhibitor	1.08	26.5	.006
Non-Oxidizing Biocide	2.02	26.7	.012
Chlorine (Cl_2)	0.10	256.7	.006
Bromine (Br_2)	3.00	63.0	.042
Carbon Dioxide (CO_2)	0.03	14,018.0	.094
TOTAL			.209

Period: 3/5/81 to 5/27/81
Flow: 4457 kgal/day

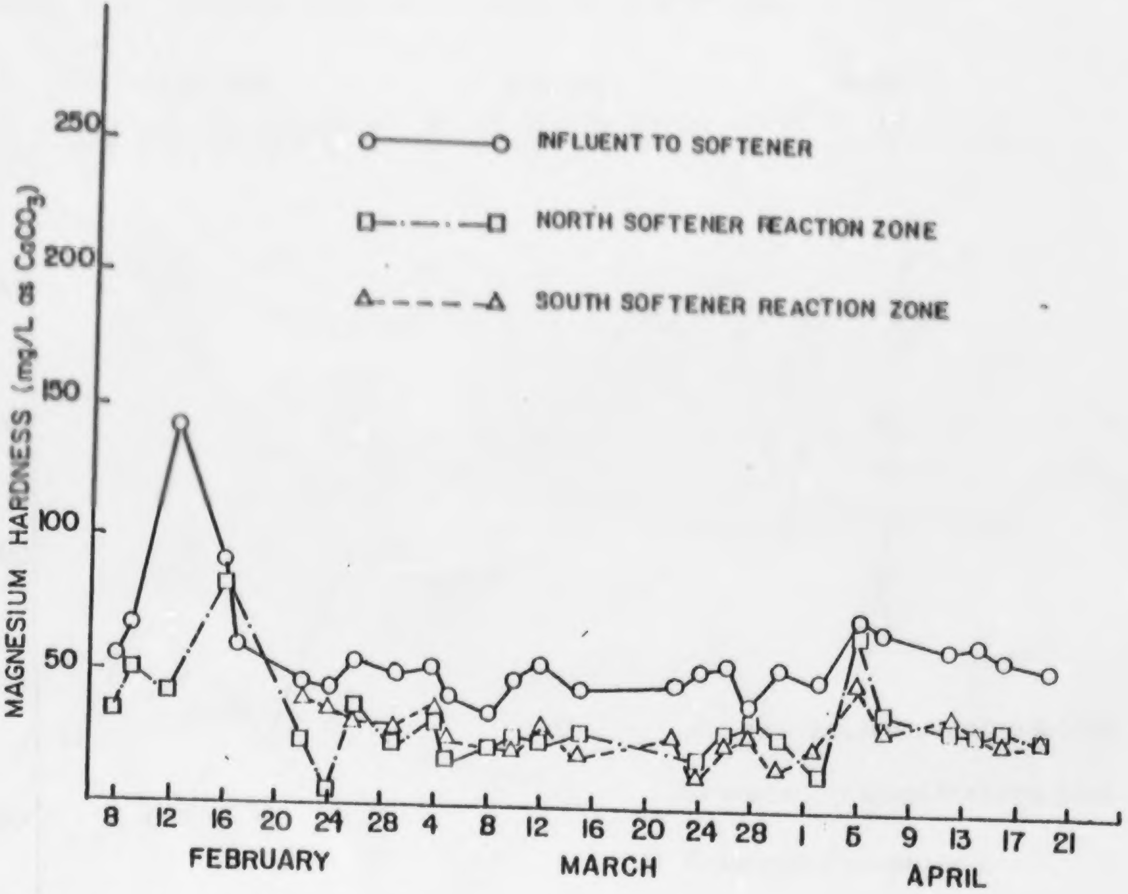


Figure 3-12. Softener influent and effluent magnesium hardess, 1981.

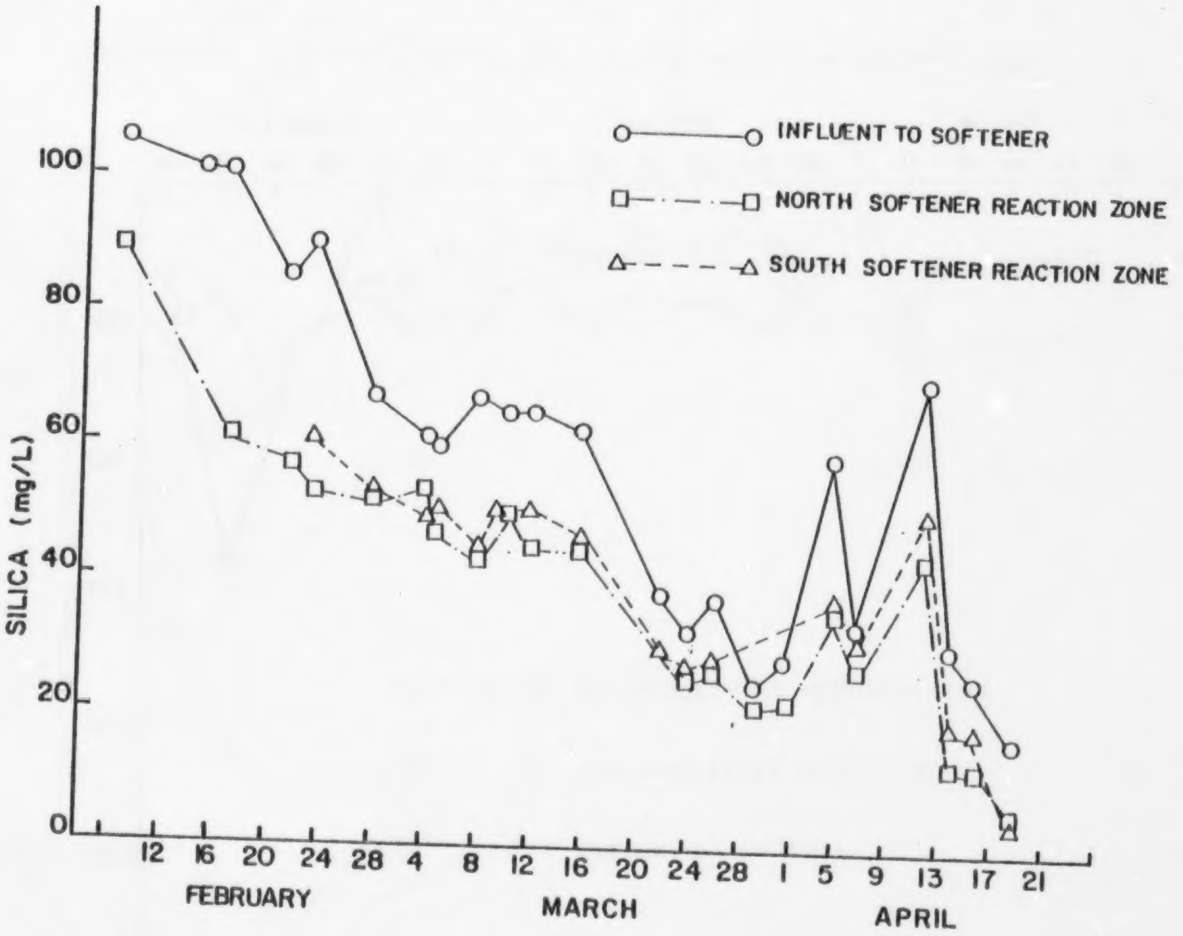


Figure 3-13. Softener influent and effluent silica, 1981.

where $(H_2CO_3^*) = (H_2CO_3) + (CO_2)_{aq}$

Since the concentration of carbonic acid may be considered negligible with respect to the concentration of dissolved carbon dioxide, the above equation reduces to

$$(CO_2)_{aq} = = \frac{(H^+)\ (HCO_3^-)}{K_1}$$

In waters of low ionic strength, at 25°C, $K_1 = 6.35$ [1]; additional constants adjusted for temperature are available in most tables. However, in cooling waters of high ionic strength, the acidity constant must be further corrected for ionic strength, e.g., by the Guntelberg approximation of the Debye-Huckel limiting law

$$pK_1' = pK_1 - \frac{0.5\ \sqrt{I}}{(1 + 1.4\ \sqrt{I})}$$

By substituting the adjusted activity constant into the above equation, the amount of CO_2 stripped out in the cooling tower (and hence the amount of CO_2 required to replace it) may be calculated simply by measuring the cooling water temperature, pH, and total alkalinity.

An example of this method of CO_2 determination can be seen in Tables 3-7 and 3-8. In Table 3-7, cooling water from the ethylene system was analyzed (for Ca^{2+}, Mg^{2+}, K^+, Na^+, Cl^-, and SO_4^{2-}) and found to have an ionic strength of 0.4986, or 0.50. Temperatures were 46°C and 32°C, and pH was 7.2 and 7.8 at the top and bottom of the cooling tower, respectively. Alkalinity was measured as follows:

1. Samples of cooling water from the top and bottom of the tower were each acidified to 4.5 with 0.02 N $H_2SO_4^{2-}$ in order to determine total alkalinity.

2. The samples were purged with air for one hour to strip out CO_2 and destroy all carbonate alkalinity.

3. After raising the pH of the sample back to its original value with 0.02 N NaOH, the samples were again tested for alkalinity--in this case, alkalinity due to organic acids, or some other non-carbonate source.

The difference between the first and second alkalinity tests yielded the carbonate alkalinity used for determination of CO_2 in cooling water, according to the procedure outlined below.

1. $$(CO_2) = \frac{(H^+)\,(HCO_3^-)}{K_1'}$$

where

$$(H^+) = \log{-1}\,(-pH)$$

$$(HCO_3^-) = 10^{-5}\,[Alk]_{CO_3}$$

$$K_1' = \log^{-1}\,(-pK_1')$$

2. $$[CO_2]_{stripped} = [CO_2]_{top} - [CO_2]_{bottom}$$

Once the amount of carbon dioxide stripped out by the cooling tower is determined (in terms of mol/L), it is simple to convert this figure to percentage CO_2 stripped, or to mg/L as $CaCO_3$. Furthermore, the feed rate of carbon dioxide required to maintain the cooling water pH may be determined by calculation of the total carbonate alkalinity removed between the top and the bottom of the cooling tower. Hence:

3. $$[CO_2]_{consumed} = 10^{-5}\,[(T_{CO_3})_{top} - (T_{CO_3})_{bottom}]$$

where

$$T_{CO_3} = [Alk]_{CO_3} + [CO_2]$$

4. $$CO_2\ \text{Feed} = [CO_2]_{consumed}\ (\text{mol/L})$$

$$\times \frac{44\ g}{mol} \times \frac{1\ lb}{454\ g} \times \frac{3.78\ L}{gal} \times \frac{50{,}000\ gal}{min} \times \frac{1440\ min}{day}$$

Table 3-8 presents similar data for cooling water for the styrene system; all calculations are performed in the same manner as for the ethylene unit. As a check on the method, the sum of the carbon dioxide consumed in the ethylene cooling tower, styrene cooling tower, and recarbonator systems was compared with the daily consumption as calculated by CO_2 inventory. Since inventory consumption was 19,000 lbs CO_2/day, and the calculated consumption was 17,962 lbs CO_2/day for a difference of 5.5 percent, the method was considered acceptable.

Hydrodynamics

As a further investigation into the actual operation of a sidestream softening system, a dye tracer study was performed on both softeners and the

TABLE 3-7. Determination of Carbon Dioxide Consumption in the Ethylene Cooling Tower System

Parameter	Cooling Tower Top	Cooling Tower Bottom
pH	7.2	7.8
T (°C)	46	32
Alkalinity (mg/L $CaCO_3$)	340.0	342.0
Non-Carbonate	51.0	85.0
Carbonate	289.0	257.0
pK_1	6.318	6.140
pK_1'	6.110	6.140
$[CO_2]$ (mg/L $CaCO_3$)	23.5	5.6

Total Carbon Dioxide Consumed = 13,163 lbs CO_2/day

Ionic Strength = 0.50
Flow Rate = 50,000 gpm

TABLE 3-8. Determination of Carbon Dioxide Consumption in the Styrene Cooling Tower System

Parameter	Cooling Tower Top	Cooling Tower Bottom
pH	7.3	7.8
T (°C)	37	25
Alkalinity (mg/L $CaCO_3$)	290	292
Non-Carbonate	40	80
Carbonate	250	212
pK_1	6.306	6.358
pK_1'	6.15	6.20
$[CO_2]$ (mg/L $CaCO_3$)	7.8	2.3

Total Carbon Dioxide Consumed = 3957 lbs CO_2/day

Ionic Strength = 0.32
Flow Rate = 15,000 gpm

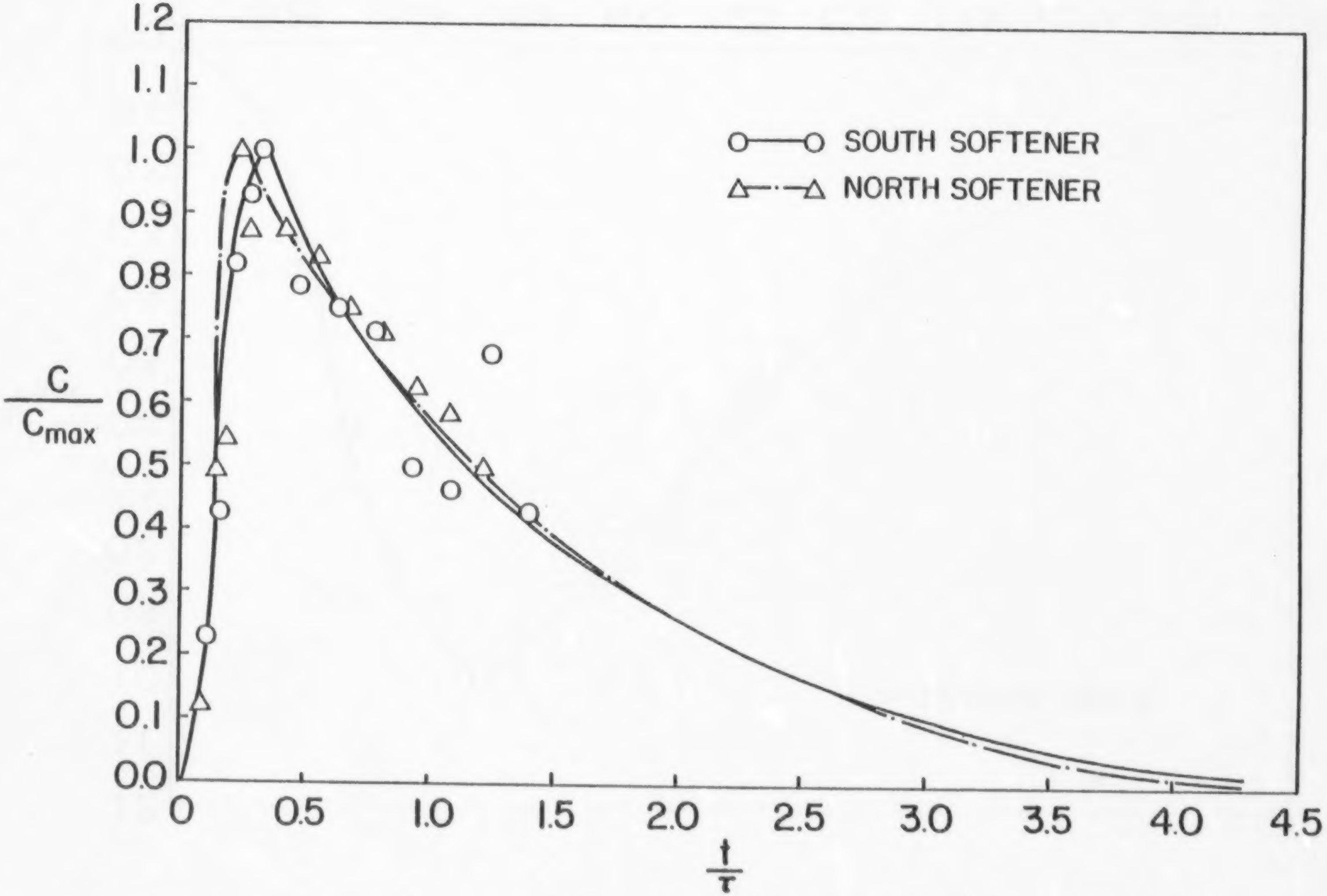


Figure 3-14. Results of dye tracer study of softener dynamics. (C_{max} = 24 ppb [North]

28 ppb [South])

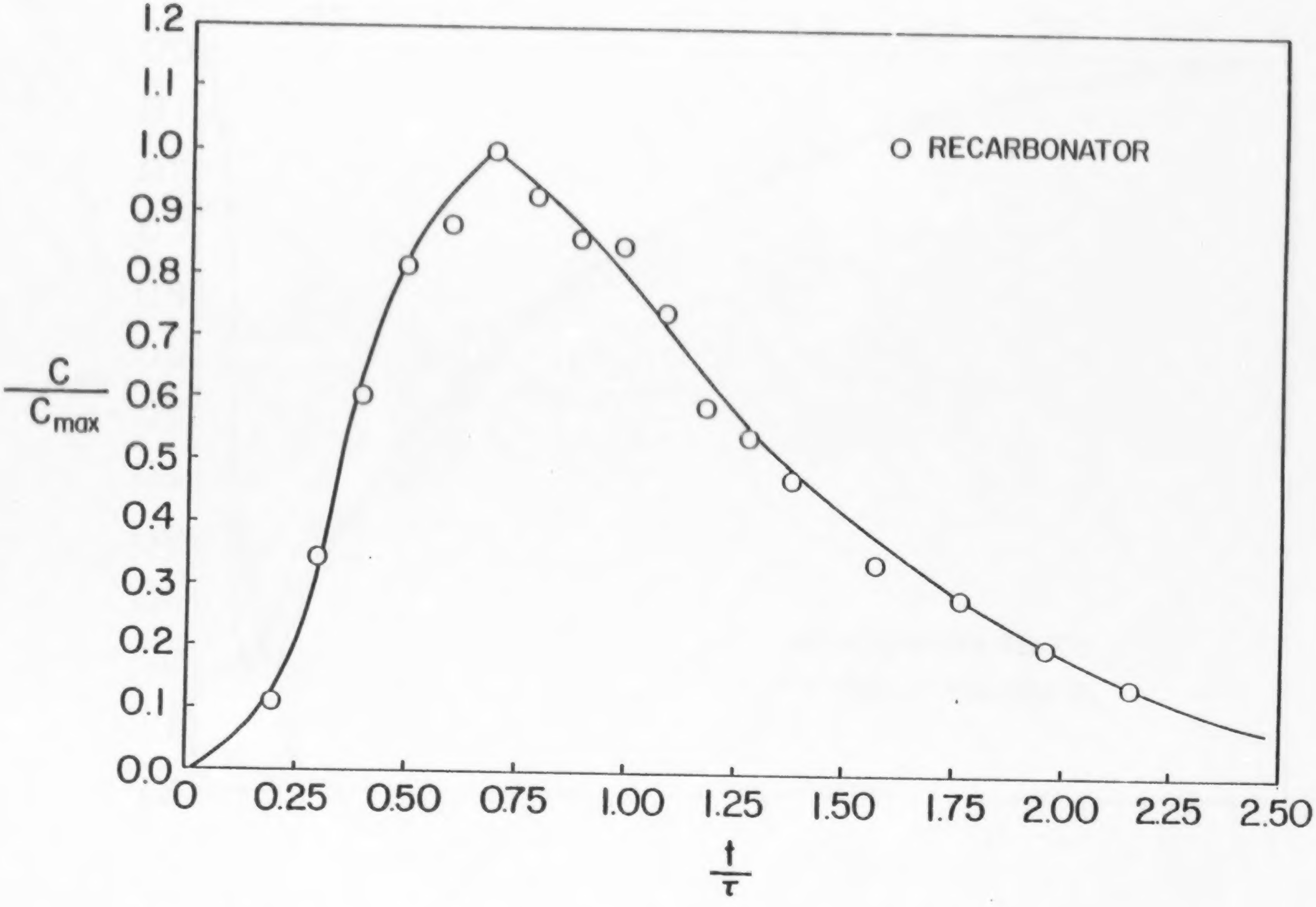


Figure 3-15. Results of dye tracer study on recarbonator dynamics. (C_{max}=430 ppb)

recarbonator to compare real and theoretical detention times. Rhodamine B dye was injected into the north and south softeners in single slugs to 24 and 28 ppb, respectively (Figure 3-14). Monitored effluent revealed immediate dispersion of the dye, with gradual elimination characteristic of a CFSTR. Observed detention times of 97 and 111 minutes compared favorably with the calculated softener detention time of 120 minutes.

Unlike the softeners, the recarbonator accepted a slug of 430 ppb which did not appear at its maximum concentration until $t/t_o = 0.5$, for a detention time of 51 minutes. The calculated detention time for the softener was 80 minutes; the profile of the recarbonator effluent (Figure 3-15) is similar to plug flow with axial dispersion.

Corrosion

Corrosion rates were monitored with mild steel coupons placed in both the etylene and styrene cooling systems. Each coupon had a surface area of 19.75 cm^2, and a density of 7.65 g/cm^3. Coupon exposure in the styrene unit varied from 26 to 221 days, and was carried out at various times between December 1979 and April 1981. On the average, penetration of the mild steel coupons amounted to 0.52 mpy, as determined by the equation:

$$P = \frac{k \times W}{A \times D \times T}$$

where P = penetration (mpy)

W = coupon weight loss (g)

A = coupon surface area (cm^2)

D = coupon density (g/cm^3)

T = exposure time (days)

k = product of all conversion constants (e.g., 365 days/year, etc.)

Final formula after substitution of all constants and coupon values was

$$P = \frac{951.1\ W}{T}$$

There was a slight problem with debris setting in the small diameter corrosion rack pipes, so the coupons were cleaned regularly with a dilute solution of 1+1 HCl. Coupon exposure in the ethylene unit was similar to the styrene unit. Average corrosion rate was 2.83 mpy. The greater penetration was attributed to the inclusion of a wastewater treatment stream with high TDS and high organic content. The increased conductivity, biological fouling, and miscellaneous impurities of the wastewater stream did contribute to the higher corrosion rate.

SECTION 3 - REFERENCES

1. Stumm, W. and Morgan, J.J. "Dissolved Carbon Dioxide," Chapter 4 in Aquatic Chemistry, 2nd ed. New York: Wiley-Interscience, 1981.

2. Gardiner, W. and Matson, J.V. "Demonstration of a Maximum Recycle Sidestream Softening System at a Petrochemical Plant," First Annual Progress Report, EPA Grant #CR 807419-01, August 11, 1981.

SECTION 4

SIDESTREAM SOFTENER PERFORMANCE

Operation of the minimal aqueous discharge sidestream softened cooling system at USS Chemicals provided numerous opportunities to study the zero discharge softener design. This chapter presents the results of three separate studies of softener performance.

The first study concerns the various measurements of alkalinity which may be used to determine the soda ash (sodium carbonate) requirements of the softener. The second study comprises investigations into the removal of silica from cooling water, including the effects of temperature, ionic strength, and magnesium concentration. The third study evaluates the effects of mixing on the softening process.

Alkalinity Determination and Softener-Efficiency

This study was conducted to improve calcium removal by using a total organic carbon (TOC) analyzer to determine the sodium carbonate (Na_2CO_3) requirements. Since soda ash (Na_2CO_3) is added to the softener to make up for any carbonate deficiency, measurement of available ionic bicarbonate determines the amount of soda ash added. At the USS Chemicals plant, ionic bicarbonate is measured by testing methyl orange alkalinity. The method used calculates carbonate on the basis of inorganic carbon determined by a TOC analyzer.

MATERIALS AND METHODS

The calcium removal in the softeners at USS Chemicals was simulated by treating actual cooling water and softener effluent from the plant in jar tests. Separate jar tests were performed with soda ash dosages based on methyl orange alkalinity, and total inorganic carbon alkalinity. The relative efficiency of these methods was determined by comparing residual calcium levels after a predetermined period of softening had occurred. An additional series of jar tests was performed to determine the relationship between lime and soda ash dosage, and the ratio of calcium to carbonate residual. A third test concerned the relative contributions of the bicarbonate ion and organic acids to total alkalinity. Finally, an economic evaluation was made to analyze the cost of improving calcium removal.

Measurements included methyl orange alkalinity (M-Alk); phenolphthalein alkalinity (P-Alk); inorganic carbon (IC); and total organic carbon (TOC); calcium, silica and magnesium concentrations, and pH of the cooling water samples. IC and TOC were measured with a Beckman Model 915A TOC Analyzer; all other tests were performed by wet chemical analysis as outlined by Standard Methods [2].

Experiment #1: Soda Ash Dosage and Calcium Removal

The first series of tests consisted of softening cooling water and softener effluent ("pre-softened") samples from USS Chemicals with soda ash dosages determined according to several different methods. In all cases, the softening procedure was as follows:

(1) Add lime to pH 10.5 and soda ash as determined.

(2) Stir mixture for at least 45 minutes to simulate full-scale softening process.

(3) Settle for 10 minutes.

(4) Filter 100 ml through 0.45μm paper filter.

Prior to softening, all samples were analyzed for calcium, alkalinity, IC and TOC, pH, and silica. After softening, the samples were analyzed for calcium alone.

In the cooling water experiments, alkalinity (P-Alk and M-Alk) and IC measurements were used to determine soda ash requirements according to the following formulae (all concentrations in ppm $CaCO_3$):

Alkalinity

$$[Na_2CO_3] = [Ca^{2+}]_{cw} + [Ca^{2+}]_{lime} - [\text{M-Alk}]$$

2(IC)

$$[Na_2CO_3] = [Ca^{2+}]_{cw} + [Ca^{2+}]_{lime} - 2[\text{IC-Alk}]$$

IC

$$[Na_2CO_3] = [Ca^{2+}]_{cw} + [Ca^{2+}]_{lime} - [\text{IC-Alk}]$$

where the subscripts cw and lime with reference to calcium indicate the calcium concentration originally present in the cooling water (as determined by analysis) and the calcium added in the form of lime, respectively. Inorganic carbon (IC) determined by TOC analysis in terms of mg C/L was converted to IC-Alk according to the following conversion formula:

$$[\text{IC-Alk}]\ (\text{ppm } CaCO_3) = \frac{\text{mg IC}}{\text{L}} \times \frac{\text{mmol C}}{\text{12 mg IC}} \times \frac{\text{mmol } HCO_3^-}{\text{mmol C}} \times \frac{\text{meq } HCO_3^-}{\text{mmol } HCO_3^-} \times \frac{\text{50 ppm } CaCO_3}{\text{meq } HCO_3^-}$$

It may be noticed that the expression mmol HCO_3^-/mmol C is equivalent to the proportionality term αHCO_3^-; hence the above formula can be abbreviated

$$[\text{IC-Alk}](\text{ppm } CaCO_3) = \frac{\text{mg IC}}{\text{L}} \times 4.17\ \alpha_{HCO_3^-}$$

No lime was added to the softener effluent, which entered the laboratory at a sufficiently high pH. Therefore, soda ash dosages for "pre-softened" samples were determined as follows:

$$[Na_2CO_3] = [Ca^{2+}]_s - \frac{[\text{IC-Alk}]}{2}$$

and

$$[Na_2CO_3] = [Ca^{2+}]_s - \frac{[\text{IC-Alk}]}{4}$$

where $[Ca^{2+}]_s$ indicates the calcium concentration of the softener effluent before the second softening reaction.

Experiment #2: Calcium/Carbonate Ratio

The second set of tests involved softening USS Chemicals cooling water with varying amounts of lime and soda ash so as to obtain different ratios of calcium to carbonate in the softener filtrate. in the first experiment, 400 mg/L lime (As $Ca(OH)_2$) raised the pH of the cooling water to 9.4-9.7, and soda ash was added from 50 - 175 mg/L (as Na_2CO_3). In the second experiment, the lime dosage was increased to 420 mg/L, which raised the pH to 10.3-10.5 while the same range of soda ash dosages were obtained. The final experiment involved various lime dosages from 450-650 mg/L, with soda ash added from 219-505 mg/L.

The softening procedure in the second set of tests was identical to that outlined above, except that in addition to effluent calcium, silica and pH were also analyzed, and the alkalinity of the filtrate was measured. Thus, carbonate after softening was determined (in ppm $CaCO_3$) as

$$[CO_3^{2-}] = [\text{P-Alk}] - [OH^-] - [SiO_2]$$

The ion activity product and saturation index were calculated for each filtrate, according to the method discussed earlier.

The results of the second set of tests were also used to estimate the contribution of organic acids to alkalinity (OA-Alk). After calculating carbonate (as above) and bicarbonate where

$$[HCO_3^-] = \frac{[H^+][CO_3^{2-}]}{K_2}$$

the organic acid alkalinity was calculated with respect to the total alkalinity such that (in ppm $CaCO_3$):

$$[\text{OA-Alk}] = [\text{P-Alk}] + [\text{M-Alk}] - [HCO_3^-] - 2[CO_3^{2-}] - [SiO_2] - [OH^-]$$

In addition, graphs derived from these results were used to obtain projections concerning the impact of lime and soda ash dosage on softener economy.

RESULTS AND DISCUSSION

TOC analyses performed over several months indicated relatively constant values of total carbon (TC), inorganic carbon (IC), and total organic carbon (TOC) for both the cooling water samples and the softener water samples, carbon ranged from 8.0 to 24.5 percent by weight (34.5-91.0 mg/L), maintaining an average of 17.8 percent IC. In the softener effluent, inorganic carbon varied between 1.8 and 7.2 percent. an average of 4.9 percent. TOC averaged 302 mg TOC/L in the cooling water, and 246 mg TOC/L for the softener effluent. As shown in Figure 4-1, nearly all of the IC present in the cooling water was removed during softening down to a level of around 10 mg IC/L. On the other hand, TOC appeared to maintain approximately the same level both before and after softening (Table 4-1).

Effect of Alkalinity Measurement on Calcium Removal

Figure 4-2 illustrates that IC-Alk is significantly lower than M-Alk, and that P-Alk is lower still. As a result, soda ash dosage (Figure 4-3) for softening the cooling water is much higher when calculated by the value of 2(IC-Alk) rather than M-Alk, and the subsequent removal of calcium (Figure 4-3) is more complete. When soda ash dosage is calculated by the still lower level of IC-Alk even more soda ash added, and more calcium is removed.

The same patterns are observed for analyses and jar tests of softener effluent samples (Figs. 4-4 through 4-7). Figure 4-6 illustrates the soda ash dosage as determined by IC-Alk/2, and the still smaller value, IC-Alk/4. As in the cooling water jar tests, the smaller alkalinity value resulted in higher soda ash dosage, and more complete calcium removal (Figure 4-7). When the initial calcium concentration in the softener effluent was low (65 ppm as $CaCO_3$), further softening did not effect significant calcium removal. Furthermore, when initial calcium concentration was greater than 90 ppm, further softening only reduced the residual to a final concentration in the range of 60 ppm.

Calcium/Carbonate Ratio in Softener Effluent

Results from the second series of experiments (in terms of percent calcium removal and final calcium/carbonate ratio) are presented in Table 4-2. The calcium/carbonate ratio was deemed significant since an excess of either calcium or carbonate in the softener filtrate was considered an indication of inefficient softening. Both calcium removal and calcium/carbonate

TABLE 4-1. TOC Analyses of Cooling Water Before and After Softening

Run #	Before Softening			After Softening		
	TOC	IC	TOC/TC	TOC	IC	TOC/TC
1	247	68	78.2	244	10	96.1
2	27	69	76.7	235	11	95.5
3	281	91	75.5	292	10	96.7
4	264	84	75.9	254	10	96.2
5	279	76	78.4	276	8	97.0

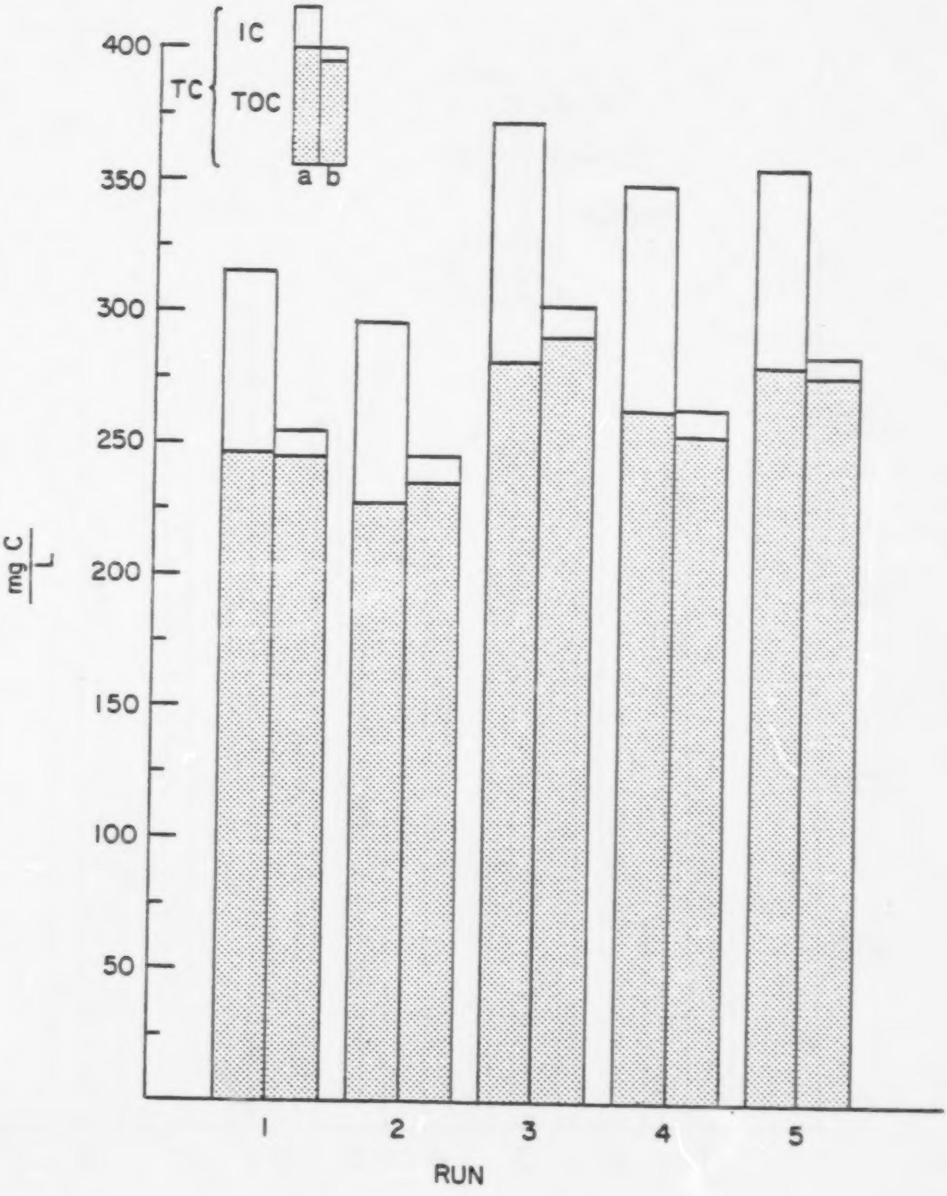


Figure 4-1. Comparison of total organic carbon (TOC) and inorganic carbon (IC) in USS Chemicals cooling water before and after softening (a = before softening; b = after softening).

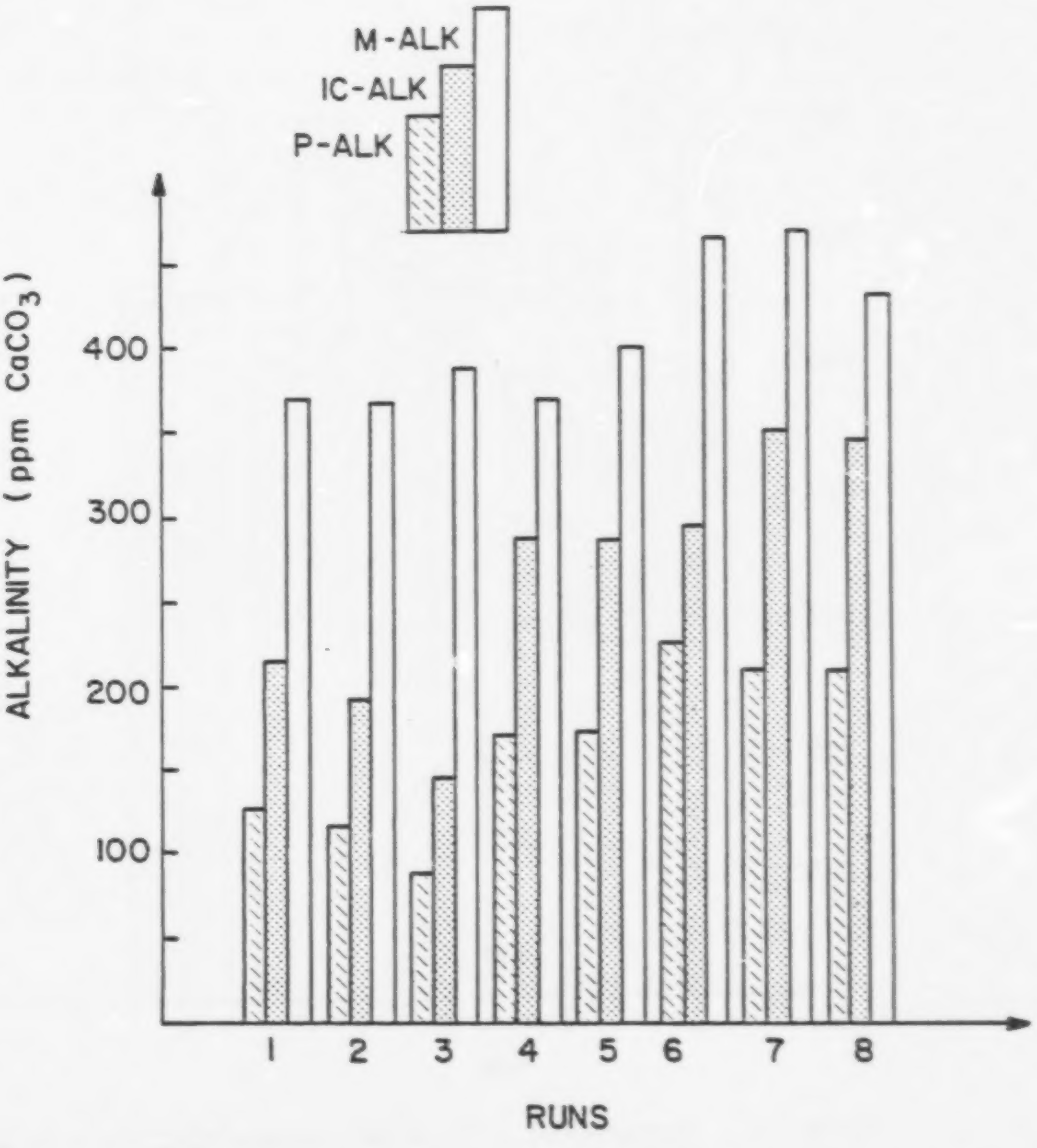


Figure 4-2. Comparison of various alkalinity measurements of USS Chemicals cooling water.

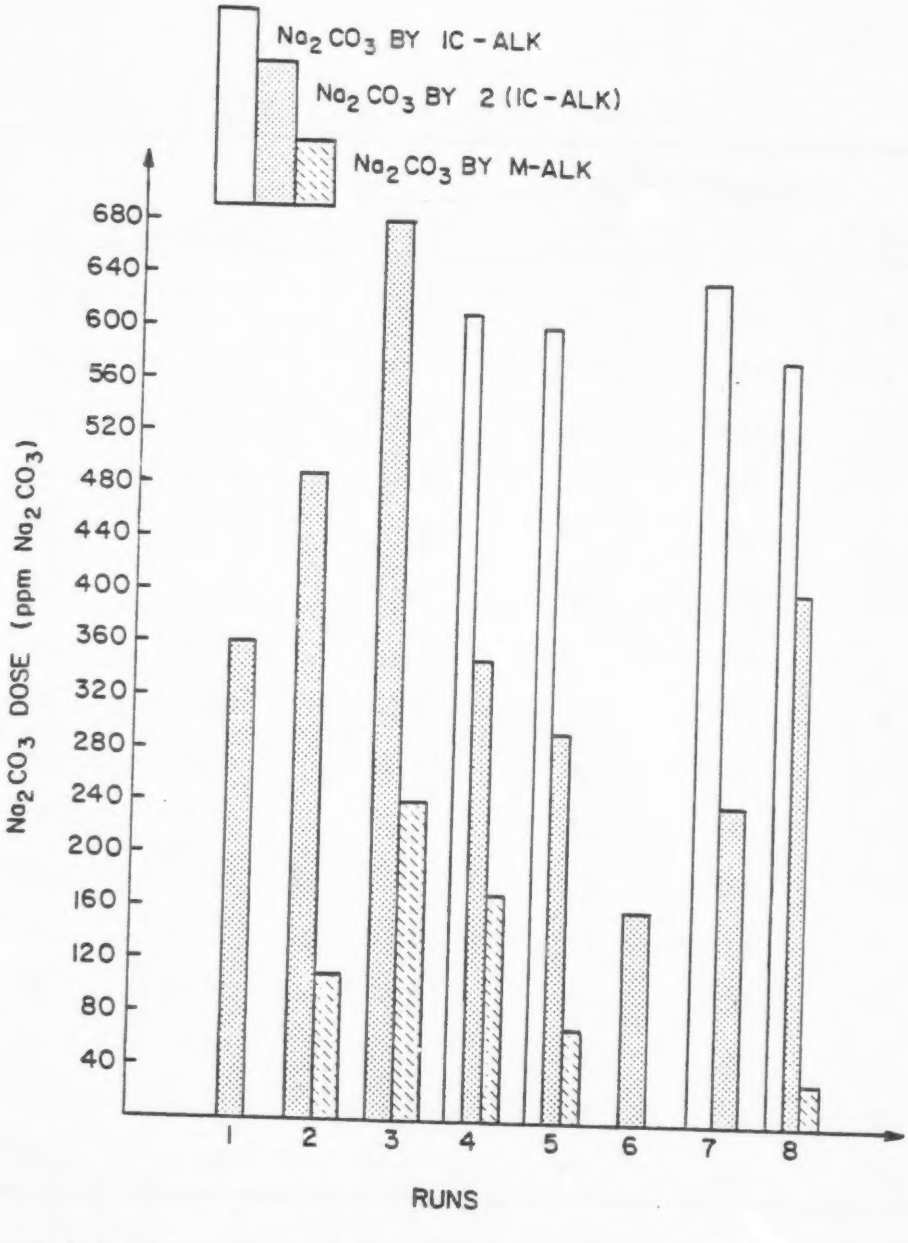


Figure 4-3. Effect of cooling water alkalinity on soda ash dosage.

TABLE 4-2. Results of $[Ca^{2+}]/[CO_3^{2-}]$ Experiments

	Dosage (mg/L)					
Test #	$Ca(OH)_2$ Added	Na_2CO_3 Added	$(\frac{[Ca^{2+}]_e}{[CO_3^{2-}]_e})$	Percent Removal	SI	Organic Acids (% T.Alk)
1	400	50	6.92	41.4	1.09	10.2
2	400	100	7.68	49.7	1.05	20.8
3	400	125	4.70	52.8	1.07	10.4
4	400	150	4.31	57.5	1.02	5.4
5	400	175	2.76	63.2	1.09	18.4
6	420	50	2.84	47.9	1.13	19.0
7	420	75	2.37	50.0	1.18	15.8
8	420	100	2.25	55.5	1.12	16.3
9	420	125	1.54	63.0	1.10	12.3
10	420	150	1.27	69.9	1.03	13.5
11	420	175	1.13	71.9	1.00	16.3
12	450	219	0.90	77.2	1.01	5.7
13	500	290	0.60	81.5	1.00	4.0
14	550	362	0.43	85.8	0.92	7.8
15	600	433	0.40	87.0	0.87	18.3
16	650	505	0.30	88.3	0.90	11.5

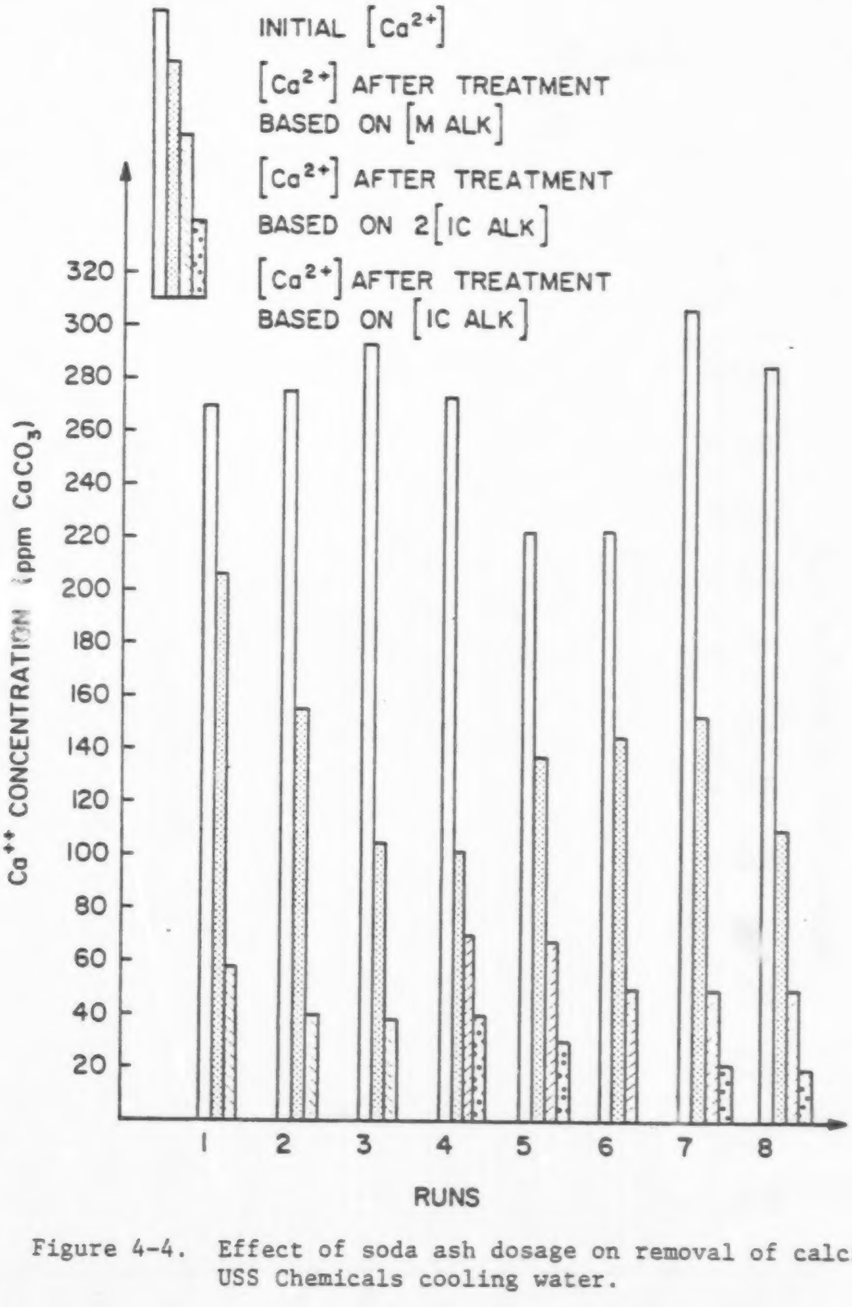


Figure 4-4. Effect of soda ash dosage on removal of calcium from USS Chemicals cooling water.

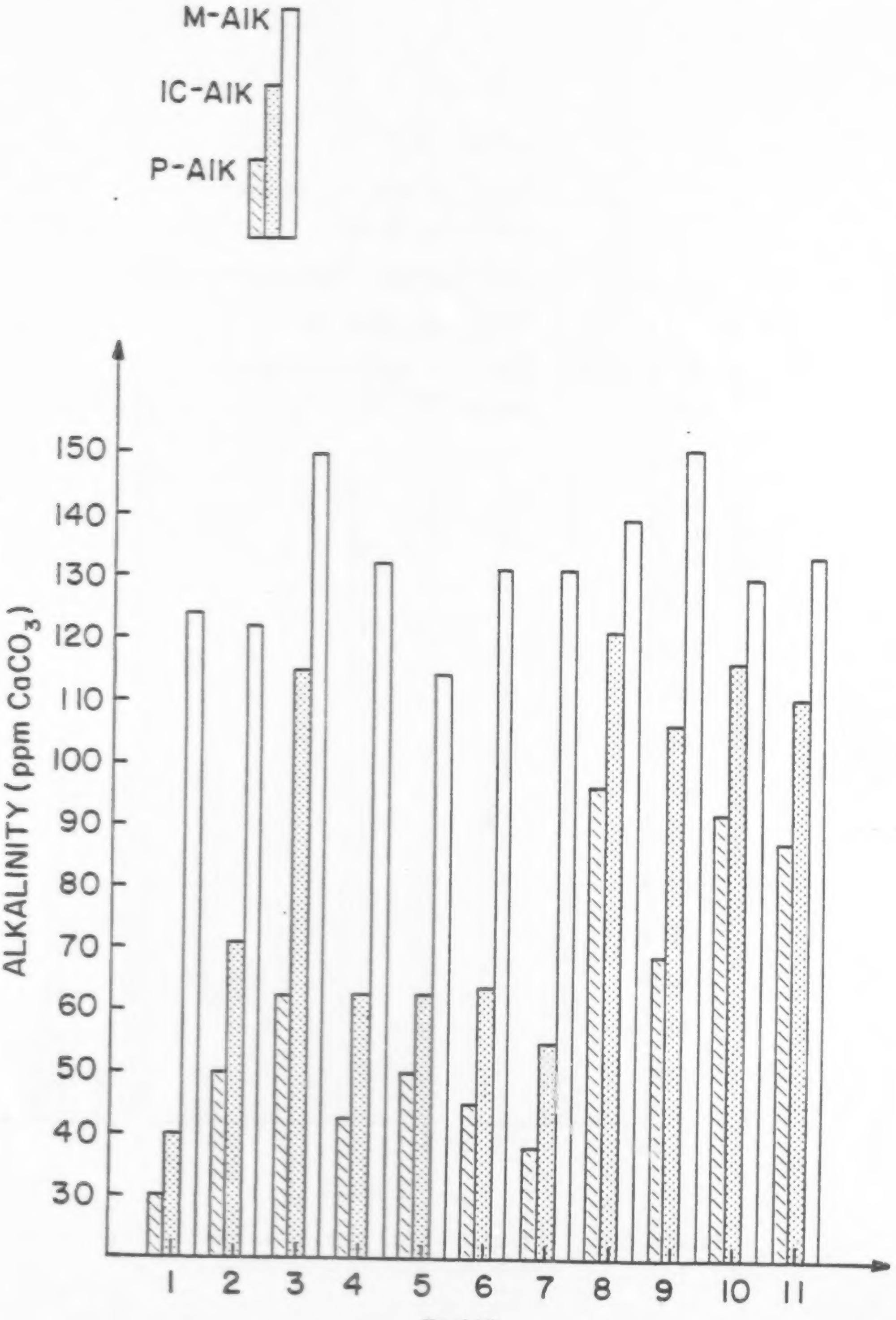


Figure 4-5. Comparison of various alkalinity measurements of USS Chemicals softener effluent.

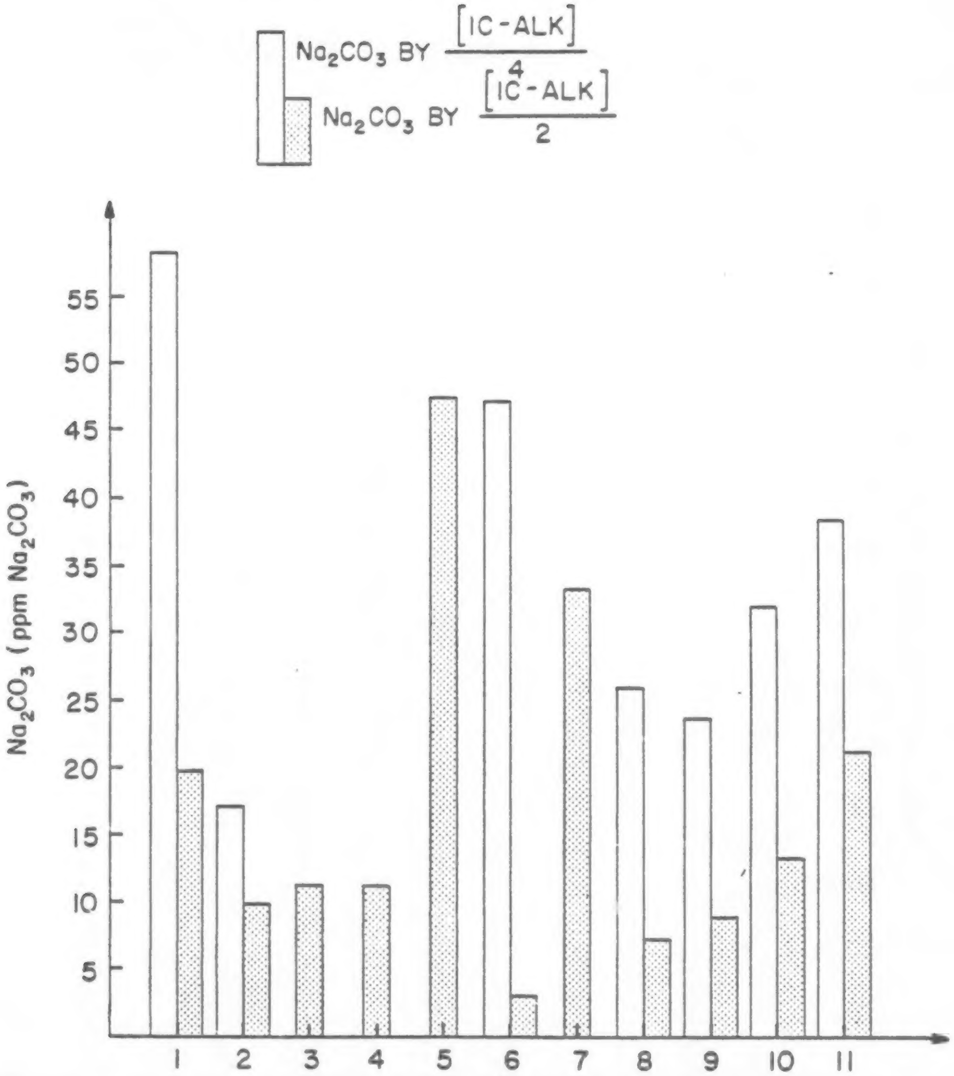


Figure 4-6. Effect of softener effluent alkalinity on soda ash dosage.

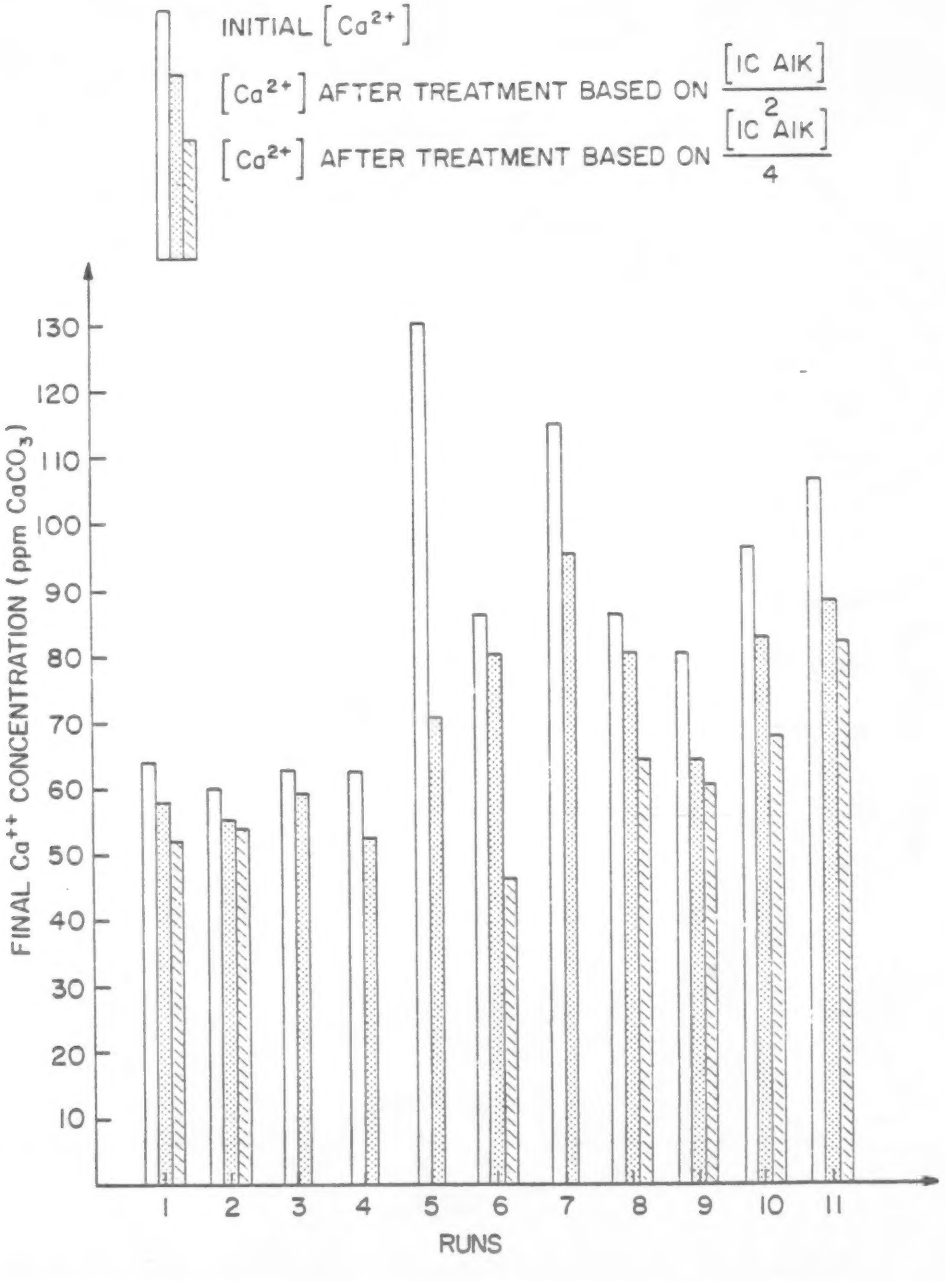


Figure 4-7. Effect of soda ash dosage on additional removal of calcium from softener effluent.

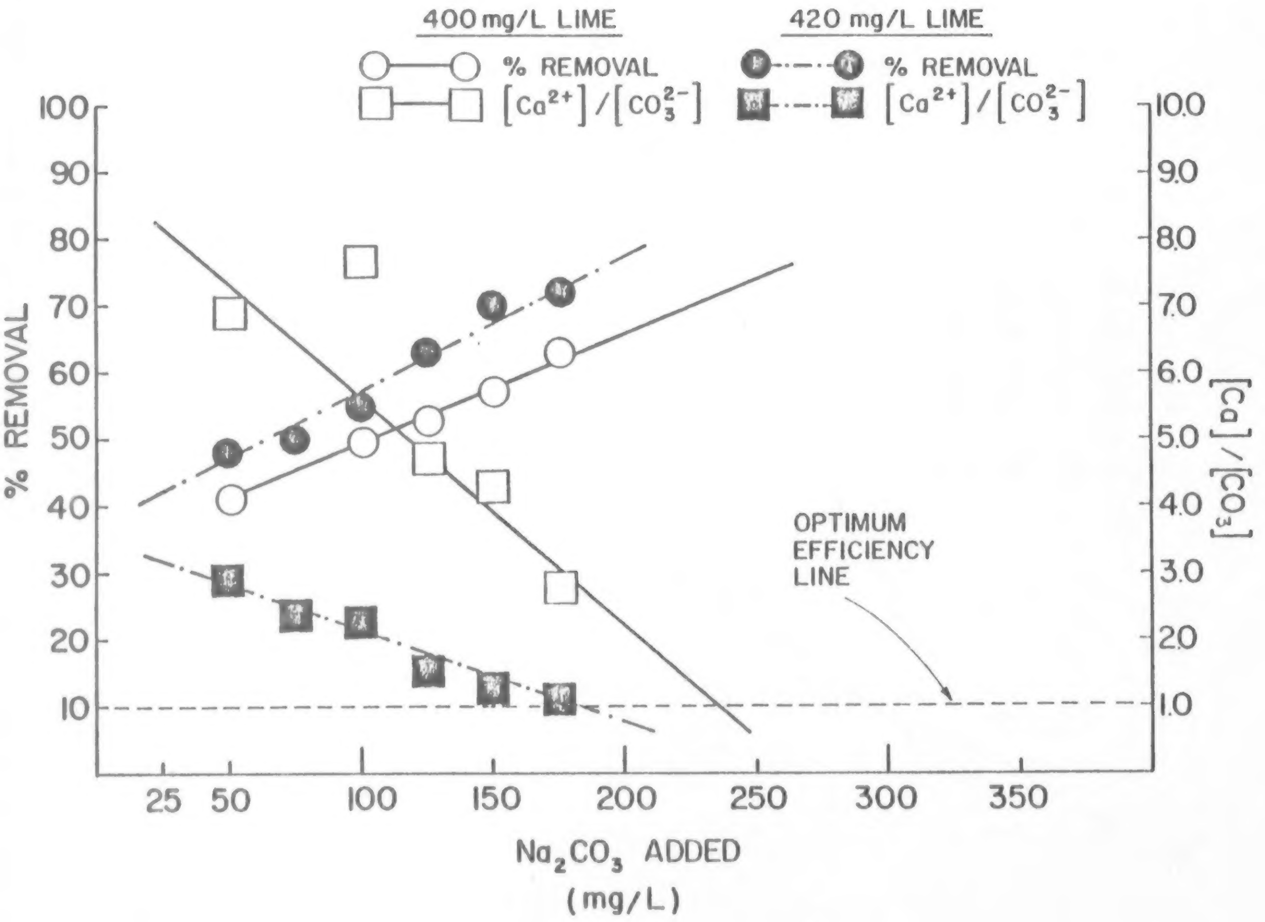


Figure 4-8. Effect of soda ash dosage on cooling water calcium removal and $[Ca]/[CO_3]$ ratio.

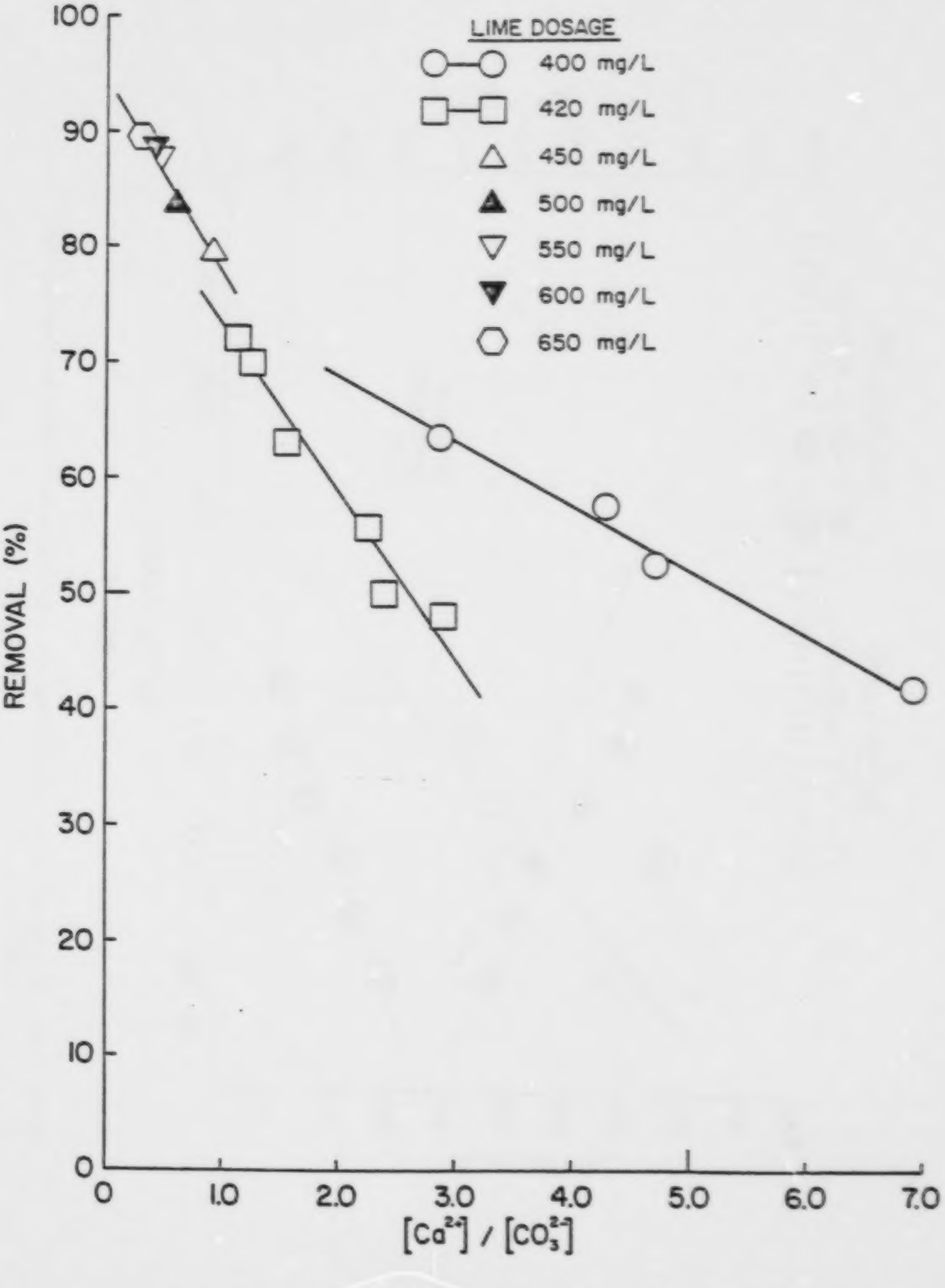


Figure 4-9. Relation between [Ca]/[CO_3] ratio and calcium removal from USS Chemicals cooling water.

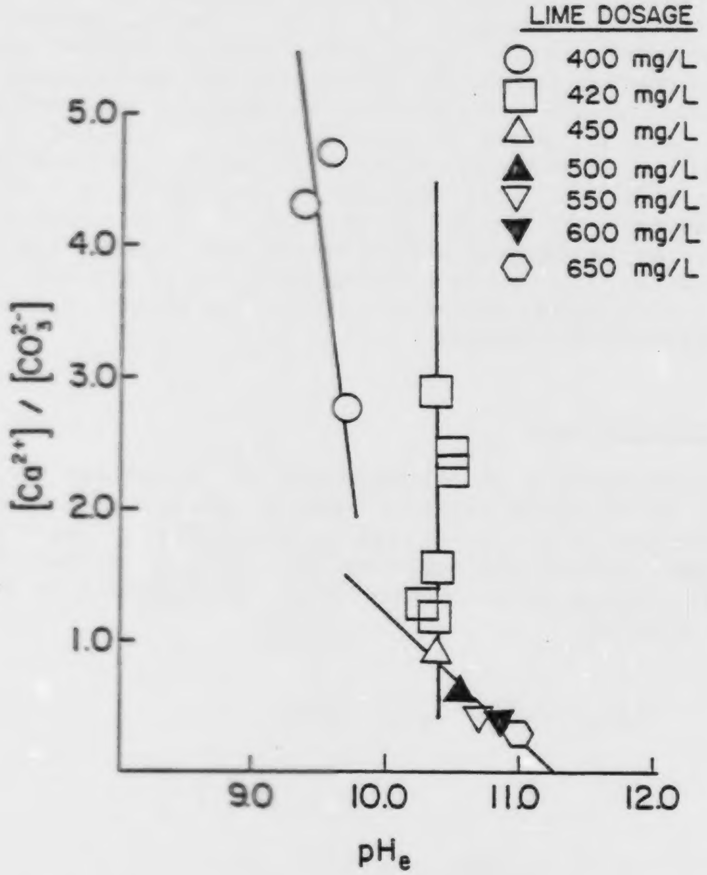


Figure 4-10. Relation between softening reaction pH and final $[Ca]/[CO_3]$ ratio.

ratio are plotted as functions of soda ash dosage in Figure 4-8. Increased lime dosage resulted in increased calcium removal for all levels of soda ash concentration. At both 400 mg/L and 420 mg/L lime, removal also improved with increased soda ash dose. Conversely, as more soda ash was added, the ratio of calcium to carbonate in the softener filtrate decreased and approached unity. This trend is also pictured in Figure 4-9, which shows calcium removal improving with decreasing calcium/carbonate ratio in the filtrate. Interestingly, despite wide variation in lime and soda ash dosage, calcium removal appears to approximate 75 percent as the filtrate calcium/carbonate ratio approaches 1.0.

Figure 4-10 plots calcium/carbonate filtrate ratios against pH, illustrating that when the softener pH reaches 10.4 - 10.5, the calcium/carbonate ratio most nearly approaches unity. Also, the solubility product constant ($K_{sp(app,\ corr)}$) and saturation index (SI) calculated for the softener filtrate at each pH indicate that the softened cooling water was well within the stability limits, and was not prone to precipitation. Calcium of free calcium (which determines, in part, the saturation index) was based on the average sulfate concentration and ionic strength of cooling water. The free calcium concentration averaged 45 percent of the total calcium concentration of the filtrate. It is probable that a portion of the organic compounds exist as acids which contribute to the total alkalinity of the water, and must be accounted or in alkalinity analyses in order to arrive at accurate measurements of carbonate and bicarbonate.

Calcium Removal and Treatment Costs

The effect of calcium removal on the economics of sidestream softening operation can be seen by relating calcium removal to softener effluent quality and sidestream flow rate for a given cooling water. The relation between softener effluent quality and softener flow rate is derived from a mass balance around the cooling tower (Figure 2-1). As explained in Section 2, this results in the equation

$$Q_mC_m + Q_sC_s = Q_dC_w + Q_sC_w$$

or

$$Q_s = \frac{Q_mC_m - Q_dC_w}{C_w - C_s}$$

Hence, for a given makeup water quality and flow, the flow from the cooling tower to the softener decreases as removal of calcium increases.

Operating costs (i.e., chemical costs) were calculated for various softener flow rates based on maintaining a cooling water calcium concentration of 267 mg/L. Constant flows and calcium concentrations were assumed as listed in Figure 4-11. Results of these computations are presented in Table 4-3. Lime and carbonate dosages were presumed to result in the same rates of removal as in jar tests 12 - 16, where initial calcium was somewhat higher (324 mg/L as $CaCO_3$).

On the basis of those assumptions, costs were calculated with calcium at 3¢/# as $Ca(OH)_2$, and soda ash at 11¢/# as Na_2CO_3 and plotted as a function of percent calcium removal in Figure 4-12. Since an increase in calcium removal rate results in a decrease in softener flow rate, a minimum cost was obtained for lime addition at the point where further addition of lime yields only minimum reductions in softener flow. On the other hand, soda ash dosage increases proportionately with calcium dosage, so no minimum was discovered.

CONCLUSIONS

Softener efficiency can be improved by basing the soda ash dosage on inorganic carbon alkalinity, as determined by the TOC analyzer. Inorganic carbon represents only 20 to 25 percent of the total carbon in cooling water, hence inorganic carbon alkalinity values are generally lower than methyl alkalinity values. As a result, the soda ash dosages calculated on the basis of IC-Alk are higher, and the calcium removal is improved.

From an operating cost standpoint, cost is proportional to the rate of calcium removal. When a given system was theoretically operated at the optimum pH for calcium removal (pH 10.4 - 10.5), operating costs escalated with improved calcium removal, despite the smaller softener flows which resulted from better quality softener effluent. This was chiefly due to the increased cost of soda ash which accompanied the addition of greater quntities of lime, since an optimum lime dosage was obtained when the softener efficiency reached 75 percent.

The most convenient parameter for estimating softener efficiency is the ratio of calcium to carbonate in the softener effluent, which approaches unity under conditions of maximum efficiency.

Removal of Silica by Sidestream Softening

Silica (silica dioxide, SiO_2) is one of the scale-forming constituents in cooling water. Research has been performed to explain the mechanism of its removal by softening, and several models have been proposed to account for silica adsorption onto magnesium hydroxide floc. In this study, the effects of different process variables upon silica removal are examined, specifically:

1) Source of magnesium precipitate

2) Proportion of silica to magnesium in the softener

3) Softener pH

4) Softener temperature

5) Concentration of total suspended solids (TSS in the softener)

In addition, results of laboratory studies of USS Chemicals cooling water and actual full-scale softener data were compared with both the Freundlich and Knight ("modified Freundlich") models for silica removal by adsorption onto magnesium hydroxide floc.

TABLE 4-3. Cost of lime and Soda Ash Based on Reduced Flow to Softener[†]

Percent Removal	$[Ca^{2+}]e$	Q_s GPM	Lime (ppm $Ca(OH)_2$)	Lime Cost	Soda Conc. (ppm Na_2CO_3)	Soda Cost[§]	Total Cost[§]
50	138	682.61	390	0.067	75	0.047	0.114
55	124.20	620.55	398	0.061	95	0.054	0.115
60	110.4	568.85	407	0.058	117	0.061	0.119
65	96.6	525.08	420	0.055	145	0.070	0.125
70	82.8	486.57	436	0.053	175	0.078	0.131
77	63.48	443.25	465	0.051	235	0.096	0.147
80	55.2	426.63	485	0.052	271	0.106	0.158
85	41.4	401.53	580	0.055	360	0.132	0.187
88	33.12	387.85	680	0.063	485	0.173	0.236

[†] Mass balance around cooling tower was computed by maintaining Ca^{2+} concentration at 276mg/L as $CaCO_3$

[§] Costs in $/gal cooling water treated

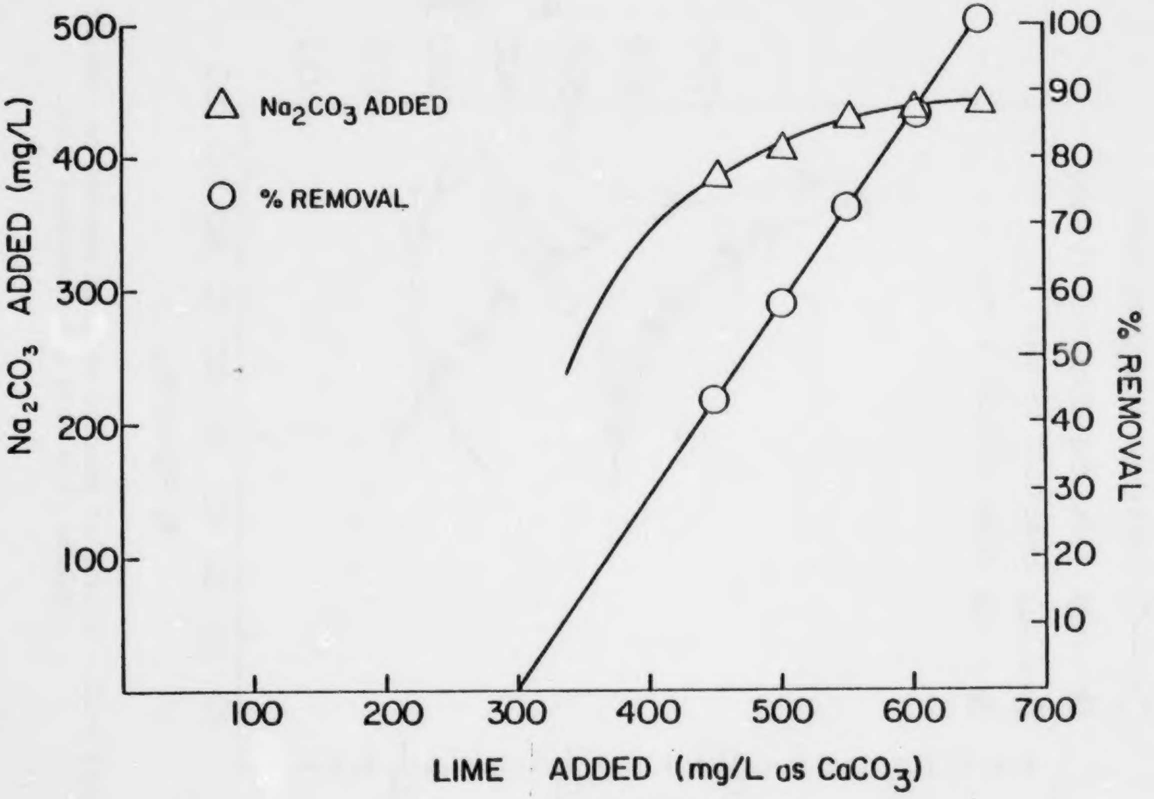


Figure 4-11. Effect of lime added on soda ash dosage and percent calcium removal.

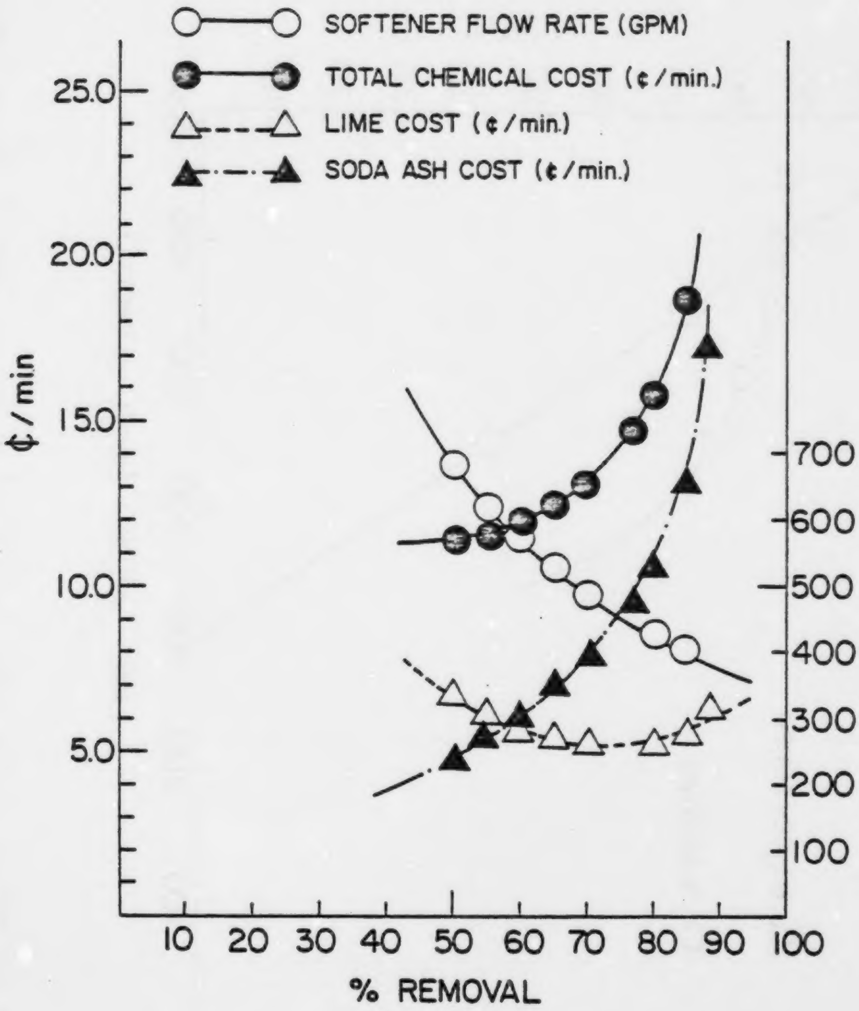


Figure 4-12. Effect of percent calcium removal on sidestream softener flow rate and treatment cost.

THEORY

The dissolution and disposition of silica in water involves hydration and dehydration reactions, as described below [4]:

$$(SiO_2)_x + 2H_2O \xrightleftharpoons[\text{dehydration}]{\text{hydration}} (SiO_2)_{x-1} + Si(OH)_4$$

Above pH 9, $Si(OH)_4$ first ionizes to form $Si(OH)_3O^-$, then (at higher pH) it forms $Si(OH)_2O_2^{2-}$. The relevant equilibrium constants (at 25°C) are as follows:

$$K_1 = \frac{[H^+][Si(OH)_3O^-]}{[Si(OH)_4]} = 1.58 \times 10^{-10} \qquad pK_1 = 9.8$$

$$K_2 = \frac{[H^+][Si(OH_2)O_2^{2-}]}{[Si(OH)_3O^-]} = 1.58 \times 10^{-12} \qquad pK_2 = 11.8$$

Silica scale differs from other precipitates (such as $CaCO_3$ and $CaSO_4$) in that its solubility increases with increasing temperature. As mentioned earlier (Section 2) relation is described by the equation

$$SiO_2 \ (mg/L) = 4.7\ T + 24$$

where SiO_2 indicates the maximum concentration of silica which will remain in solution at a given temperature T (°C) [5].

Silica scale is formed by polymerization of dissolved silica which results in an amorphous colloid. This colloid has a high affinity for di- and trivalent cations, which are nearly always found in scale samples. the lime softening process takes advantage of this affinity by exposing the silica to ionic magnesium (Mg^{2+}) at high pH. As a result, one reaction which has been proposed to describe the mechanism of silica removal is as follows:

$$Si(OH)_4 + (OH^-) \rightleftharpoons Si(OH)_3O^- + H_2O$$

$$Si(OH)_3O^- + Mg(OH)_2 \rightleftharpoons Mg(OH)_2\text{—}Si(OH)_3O^-$$

Previous studies also indicate that the removal of silica by magnesium hydroxide floc is better characterized as adsorption, rather than a stoichiometric chemical reaction. As such, it is often described by the Freundlich isotherm model

$$q = \frac{x}{m} = kC^{1/n}$$

where k and n are constants, q is the adsorption of silica onto magnesium hydroxide floc on a weight/weight basis, and C is the final concentration of silica in solution.

Empirical data of silica adsorption applied to the Freundlich model is usually analyzed according to the linearity of a plot of log (x/m) versus log C. According to the linearized Freundlich equation log, ((x/m) = log K + 1/n) log C. However, Knight [4] has proposed a modification of this model, replacing the final concentration of silica (C) with the "log mean concentration" term (LMC) such that

$$(\frac{x}{m}) = k' \, (LMC)^{a'}$$

where

$$LMC = \frac{C_i - C_f}{\ln(\frac{C_i}{C_f})}$$

C_i = initial silica concentration

C_f = final silica concentration

Knight's model is particularly useful, in that it accounts for any variation of adsorption intensity which may occur as the initial silica concentration is depleted during the course of the adsorption process. Its main drawback is that when the equation is used to predict the extent of adsorption, the final silica concentration must be estimated in advance.

In Figure 4-13 [7], shows silica concentration in cooling water effluent as a function of magnesium concentration prior to reaction.

MATERIALS AND METHODS

Four different kinds of jar tests were designed to study different aspects of silica removal. The first two tests involved laboratory-prepared solutions of silica and magnesium in deionized water (DI H_2O), while the second two tests were conducted with actual cooling water obtained from USS Chemicals. In addition, full-scale tests were performed by varying conditions at the softeners of USS Chemicals.

Experiments with Deionized Water

The first jar test was designed to determine the relative effectiveness

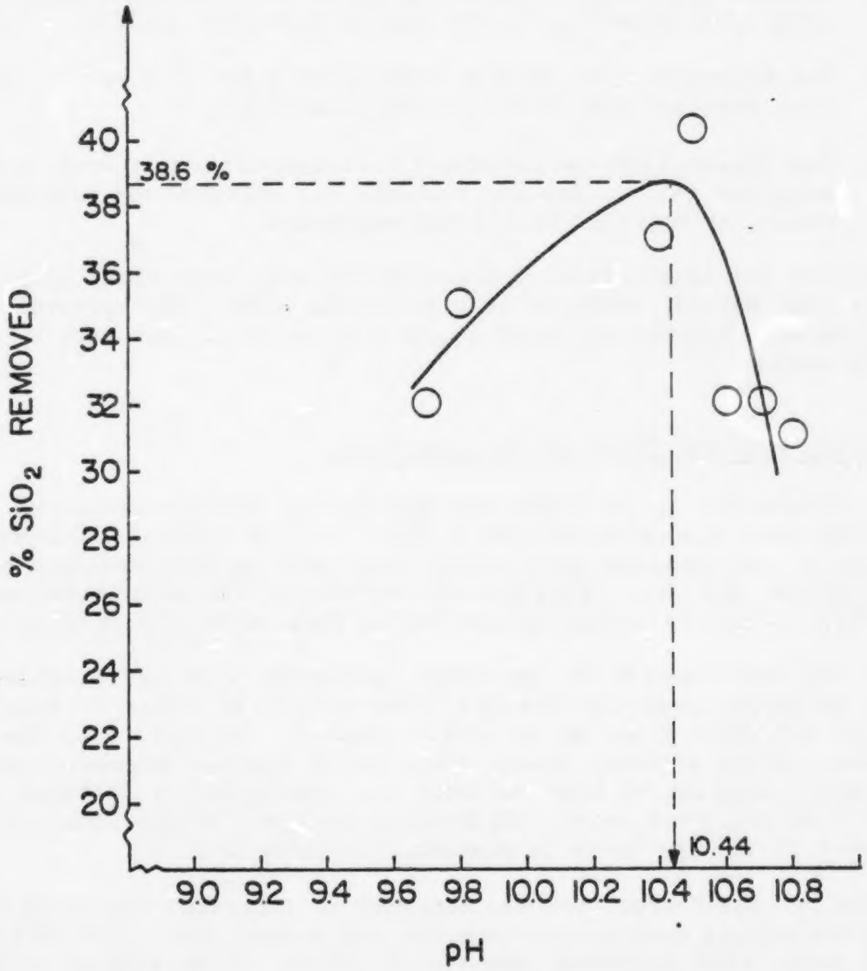


Figure 4-13. Effect of softener pH on silica removal.

of different compounds as sources of magnesium for silica removal. In this study, separate solutions of 60 mg SiO_2/L (from sodium metasilicate) were treated with 50 mg/L magnesium from MgO and $Mg(OH)_2$, respectively. The lime softening process was simulated as follows:

1) 500-ml aliquots of silica solution were placed in 2-L beakers, to which were added magnesium from either compound.

2) Calcium was added to raise the pH to 10.4; soda ash requirement was calculated according to the method described earlier.

3) The solutions were stirred continuously for 45 minutes, after which they were allowed to settle for 15 minutes.

4) The flasks were decanted and filtered through a 0.45 m Millipore membrane filter, and the filtrate was analyzed for relevant constituents, principally silica and magnesium.

Initial and final silica concentrations were determined by the molybdosilicate blue method; analyses were performed with a B&L Spectronic 20 Spectrophotometer. Initial and final magnesium concentrations were determined by the EDTA method.

Experiments with USS Chemicals Cooling Water

The second set of jar tests was designed to develop isotherms for silica adsorption onto magnesium hydroxide floc. Silica removal followed the same procedure as the previous test, except that only $Mg(OH)_2$ was used as a source of magnesium, and the magnesium concentration was maintained at 16.75 mg Mg/L. Initial silica concentration varied from 40 to 120 mg SiO_2/L.

In the third series of jar tests (performed with USS Chemicals cooling water), lime and soda ash dosages were varied in order to determine the effect of different final pH on silica removal. In this case, the source of magnesium was the softener sludge which had an average magnesium content 12.7 mg/L. After addition of lime and soda ash, the procedure followed was identical to that followed above. An average analysis of USS Chemicals cooling water used in the jar tests is presented in Table 4-4.

Finally, the fourth test was designed to determine the equilibrium isotherms for silica adsorption from cooling water, and involved spiking the cooling water with different amounts of silica to an initial concentration varying from 43.8 to 163.8 mg SiO_2/L.

It should be noted that the initial laboratory tests which were performed with USS Chemicals cooling water yielded results which were not easily reproduced, due to extensive spectrophotometric interference by the intense yellow color of the water. Subsequent analysis indicated that the interfering color was produced by an average of 25 mg CrO_4^{2-}/L and organic acids equal to about 15 percent of total alkalinity. In order to eliminate this interfer-ence, all cooling water used in laboratory tests was treated with ferrous sulfate ($FeSO_4 \cdot 7H_2O$) and powdered activated carbon (PAC), prior to silica removal.

In addition to the laboratory-scale tests, full-scale studies were per-

TABLE 4-4. Average Initial Characteristics of the USS Chemicals Water for Jar Tests

---

pH: 8.1

Alkalinity

P = 0

M = 377 ppm as $CaCO_3$

Hardness

Total	357 mg/L as $CaCO_3$
Ca^{2+}	305 mg/L as $CaCO_3$
Mg^{2+}	52 mg/L as $CaCO_3$

Silica (SiO_2)

44 mg/L

formed by measuring influent and effluent silica and magnesium at the North and South Softeners of the USS Chemicals plant under a variety of conditions. In the first study, silica removal was determined in the presence of various concentrations of suspended solids--from 22,000 to 59,000 mg/L--in order to observe the effect of TSS on the efficiency of silica adsorption. Also, influent and effluent concentrations of both silica and magnesium were measured under stable conditions to determine the optimum ratio of silica to magnesium with respect to final silica concentration. Finally, variable speed mixers were installed in the North Softener, and the effects of various mixing speeds were examined over a period of four months.

Determination of the effect of temperature on silica removal was obtained by a comparison of results reported in the literature by various researchers, whose referenced works should be consulted for procedural details.

RESULTS AND DISCUSSION

Effects of Different Magnesium Sources on Removal of Silica

Results of the silica removal jar tests performed with different magnesium compounds are summarized in Table 4-5. As can be seen, no real difference between $Mg(OH)_2$ and dolomitic lime ($Ca(OH)_2 \cdot MgO$) was observed with respect to removal of silica. However, when magnesium must be added to cooling water to remove silica, $Mg(OH)_2$ may be preferred to dolomitic lime, since the latter introduces excessive quantities of calcium. This additional calcium may in turn require additional soda ash for effective softening, thereby increasing alkalinity. Furthermore, as discussed above, when the pH is raised above the optimum for silica removal, SiO_2 may redissolve, increasing the silica residual.

Effect of pH on Removal of Silica

Since the solubility of silica increases with pH, it was suspected that there should be an optimum pH at which the highest percent removal of silica occurs. Jar tests conducted at 25°C with 20,000 mg/L suspended solids from softener sludge as a source of magnesium (Figure 4-15) indicate that pH 10.45 was the optimum pH for removal of silica from USS Chemicals cooling water.

Effect of Total Suspended Solids on Silica Removal

A four-month study of full-scale sidestream softening operations at USS Chemicals included continual monitoring of the softener suspended solids (TSS), as well as influent and effluent concentrations of silica and magnesium. Results of this study, as regards the effect of suspended solids on silica removal, are summarized in Figure 4-16. As expected, increasing the TSS resulted in increased removal of silica, since the suspended solids contained approximately 15 percent magnesium (by weight).

However, while full-scale removal improved as the TSS concentration increased to nearly 60,000 mg/L, the percent removal obtained in the laboratory at 20,000 mg TSS/L was roughly double that obtained in the full-scale plant at the same level of suspended solids.

TABLE 4-5. Comparison of Magnesium Source for Silica Removal

Magnesium Compound Used	Initial Mg ppm as $CaCO_3$	Final Mg ppm as $CaCO_3$	Initial SiO_2 ppm	Final SiO_2 ppm	Percent SiO_2 Removed
MgO	50	0	60	29	52
$Mg(OH)_2$	50	0	60	31	48

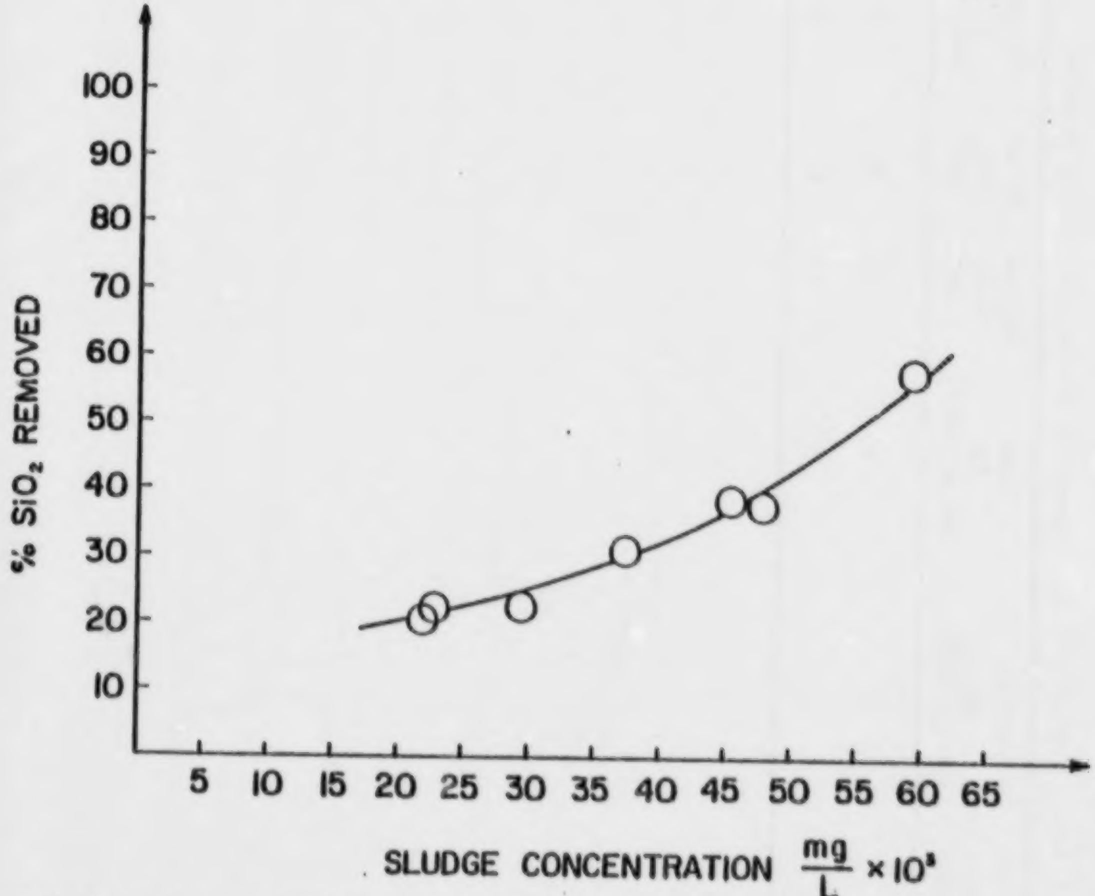


Figure 4-14. Effect of softener sludge TSS on silica removal.

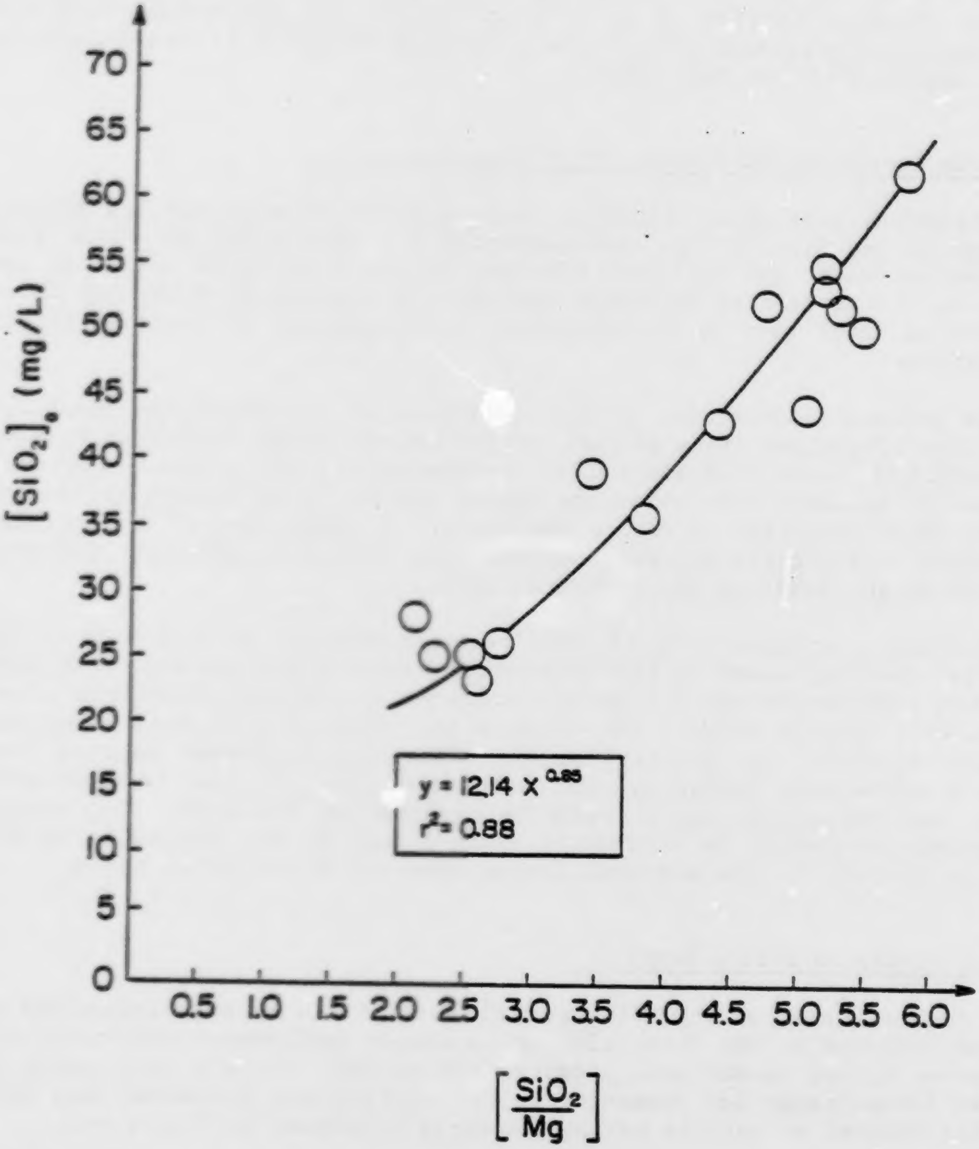


Figure 4-15. Effect of silica/magnesium ratio on silica removal.
Mg_i = 12.5 mg/L T = 112 °C pH = 10.4

Effect of SiO_2/Mg Ratio on Silica Removal

In Figure 4-17, effluent silica concentration is plotted as a function of the ratio of silica (as mg SiO_2/L) to magnesium (as mg Mg/L) in the softener influent at USS Chemicals. As can be seen, as the SiO_2/Mg ratio increases beyond 2.5, more and more silica remains dissolved in the softener effluent. Final selection of an optimum SiO_2/Mg ratio requires both the determination of maximum effluent silica concentration allowable and an economic analysis of relevant costs.

Equilibrium Isotherms and Models for Silica Adsorption

Equilibrium isotherms, relating final silica concentration (mg SiO_2/L) to adsorption (mg SiO_2/mg Mg), are presented for laboratory jar tests with both deionized water and USS Chemicals cooling water in Figure 4-18. As can be seen, silica appears to be better adsorbed by magnesium in the USS Chemicals cooling water than in the deionized water samples, at least at higher concentrations.

This increased adsorption is also reflected in the adsorption equations derived from linearized plots of both Freundlich and Knight (modified Freundlich) models (Figures 4-19 and 4-20). Parameters of the derived equations are presented in Table 4-6, where the higher 1/n and (1/n)' values correspond to an increased intensity of silica adsorption. A comparison of the correlation coefficients for the different models also reveals a generally improved fit of the Knight model to the empirical data.

A further comparison can be made between removal of silica from USS Chemicals' cooling water in the laboratory, and adsorption obtained when silica was removed in the full-scale softener at the USS Chemicals plant (Figures 4-21 through 4-23). The exponential terms in both the Freundlich and Knight equations are greater for the adsorption isotherms derived from full-scale operations, indicating that laboratory data may tend to underestimate the adsorption that may actually be obtained in the field. One reason for improved adsorption by full-scale methods may be the continuity of the process in contrast to the non-equilibrium behavior of the batch tests.

Effect of Mixing on Silica Removal

At the beginning of 1982, two variable speed mixers were installed in the North Softener at USS Chemicals, and softener performance was monitored at different mixing speeds over a four-month period. While a full report of variables investigated are presented below, equilibrium isotherms developed for silica removal at various mixing speeds is presented in Figure 4-24.

While these curves depart from the standard isotherm forms derived earlier in the laboratory and in the South Softener, it appears that greater adsorption was obtained at higher rpm. However, further research in this area is required in order to develop more consistent data.

TABLE 4-6. Freundlich and Knight Isotherm Parameters for Adsorption of Silica onto Magnesium Hydroxide Floc

Freundlich: $q_e = K(C_e)^{1/n}$

Knight: $q_e = K'(LMC)^{(1/n)'}$ where $LMC = \frac{C_i - C_e}{\ln (\frac{C_i}{C_e})}$

	Freundlich			Knight		
Water	K	1/n	r^2	K	(1/n)'	r^2
DI H_2O	.688	.255	.8843	.52	.305	.9051
USS Chemicals Cooling Water	.098	.788	.9754	.091	.772	.9817
South Softener	.084	.898	.6994	.049	1.00	.7877

CONCLUSIONS

In summary, experiments in the laboratory indicated that silica may be removed equally effectively with either $Mg(OH)_2$ or MgO as the source of magnesium. Silica is removed most efficiently when the pH in the softener is raised to 10.4 - 10.5. Furthermore, removal of silica improves with increased contact time and higher temperature. Studies performed with full-scale softener operation show that silica removal is improved at higher concentrations of suspended soliids which contain magnesium (i.e., softener sludge). Also increased mixing speeds may tend to improve silica adsorption, but this area must be studied further.

Isotherms developed from both laboratory-scale and full-scale experiments suggest that, in general, adsorption in full-scale, continuous process softeners exceeds that of laboratory batch reactors (i.e., jar tests). This tendency should be considered whenever laboratory isotherms are applied to full-scale processes for design purposes.

The Effect of Mixing Speed on the Softening Process

The zero-discharge sidestream softening system currently operating at the USS Chemicals plant uses two Infilco softeners, called to as the North and South Softeners. In this study, the effect of variable mixing in the first chamber of the reaction zone was investigated by means of two turbine mixers (Eurodrive Inc. Type REGO D11 BD1 80 N4C) installed in the North Softener. As mentioned earlier, South Softener remained unmodified, as a control, for the purpose of comparison.

MATERIALS AND METHODS

To determine the effects of mixing on the North Softener (as compared with the slow-mixed, unmodified South Softener), grab samples were collected from different sampling locations in both softeners on a regular basis (Figure 4-25). All water samples were analyzed in the Environmental Engineering Laboratories at the University of Houston according to Standard Methods, 15th Edition.

Determination of the effect of mixing on softening efficiency was divided into three different parts, and the corresponding work was performed during three periods. During the first period (eight weeks), the various parameters were measured every other day in both softeners and the plant operators performed alkalinity, pH, and calcium hardness measurements four times a day. The data collected were used as the baseline of comparison between the modified and unmodified softeners. In the second period, the two mixers were installed in the North Softener, and the plant operators were trained to adjust the softeners so that both softeners received the same flow rate, and dosages of lime and soda ash. During the third period, the efficiency of the modified softener was tested at various first chamber mixing rates. In these tests, the modified softener turbine mixer speed was varied while the flow rate, and lime and soda ash dosages, recirculation rate, and sludge blowdown for both softeners were kept the same. Four different mixing speeds were tested--30, 40, 50, and 70 rpm. Each mixing speed was maintained until steady state condition was reached, except for 30 rpm, since it was found that at 30 rpm mixing was inadequate for a satisfactory equipment response.

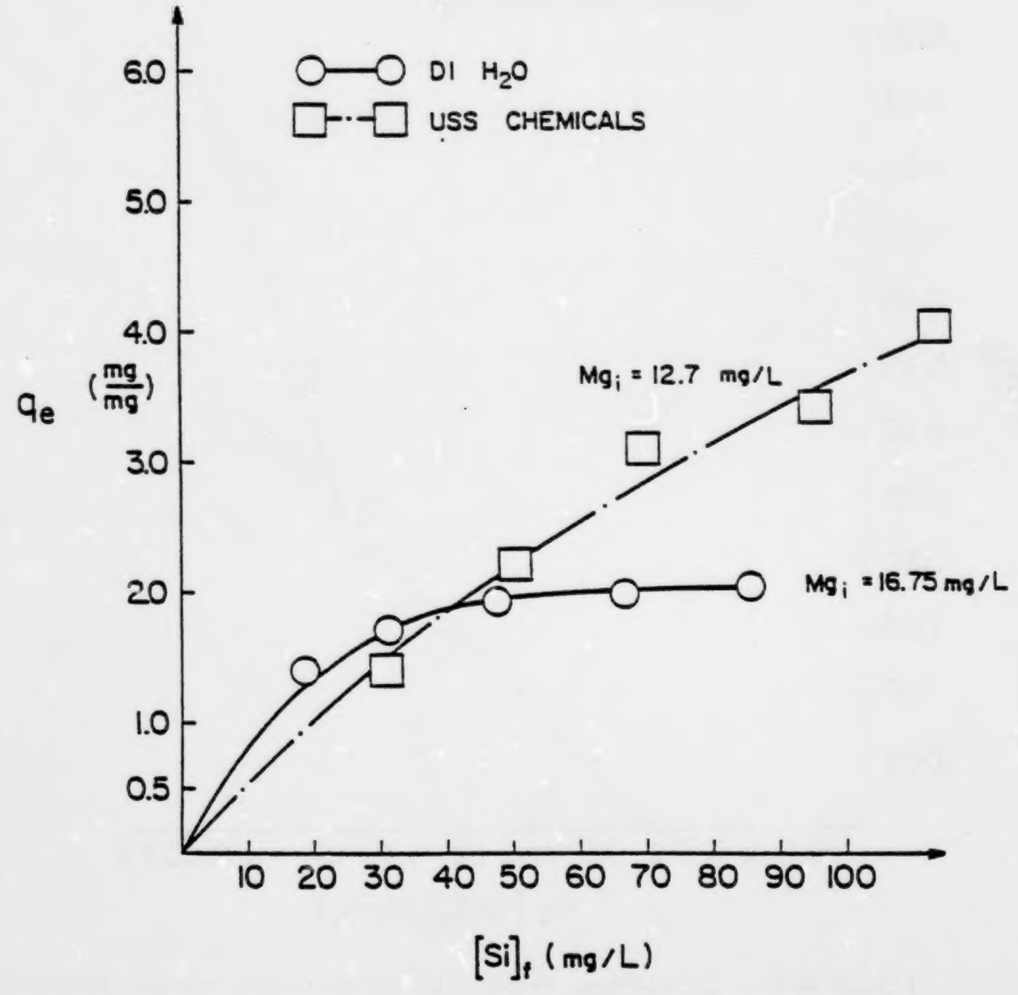


Figure 4-16. Equilibrium isotherm for adsorption of silica onto magnesium hydroxide floc.

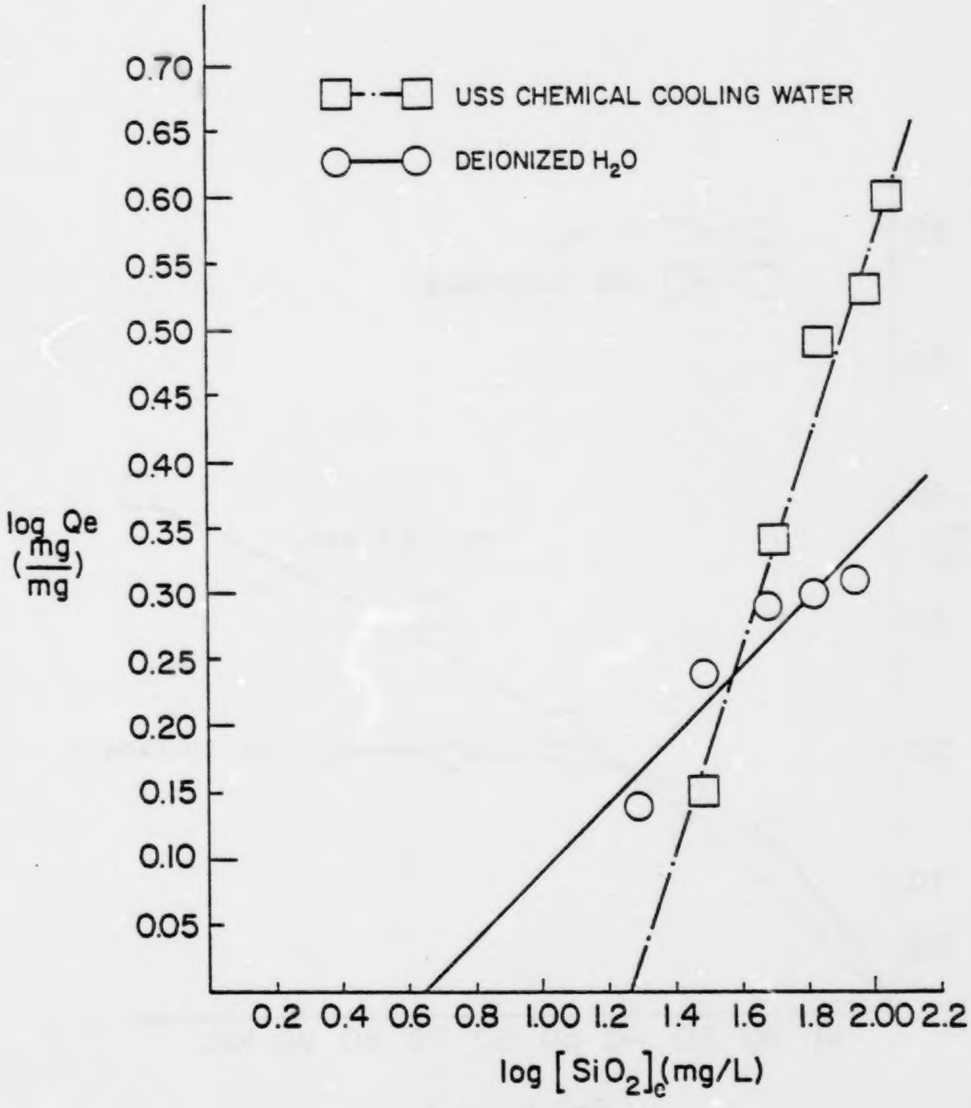


Figure 4-17. Linearized Freundlich isotherm for silica adsorption (Jar Tests).

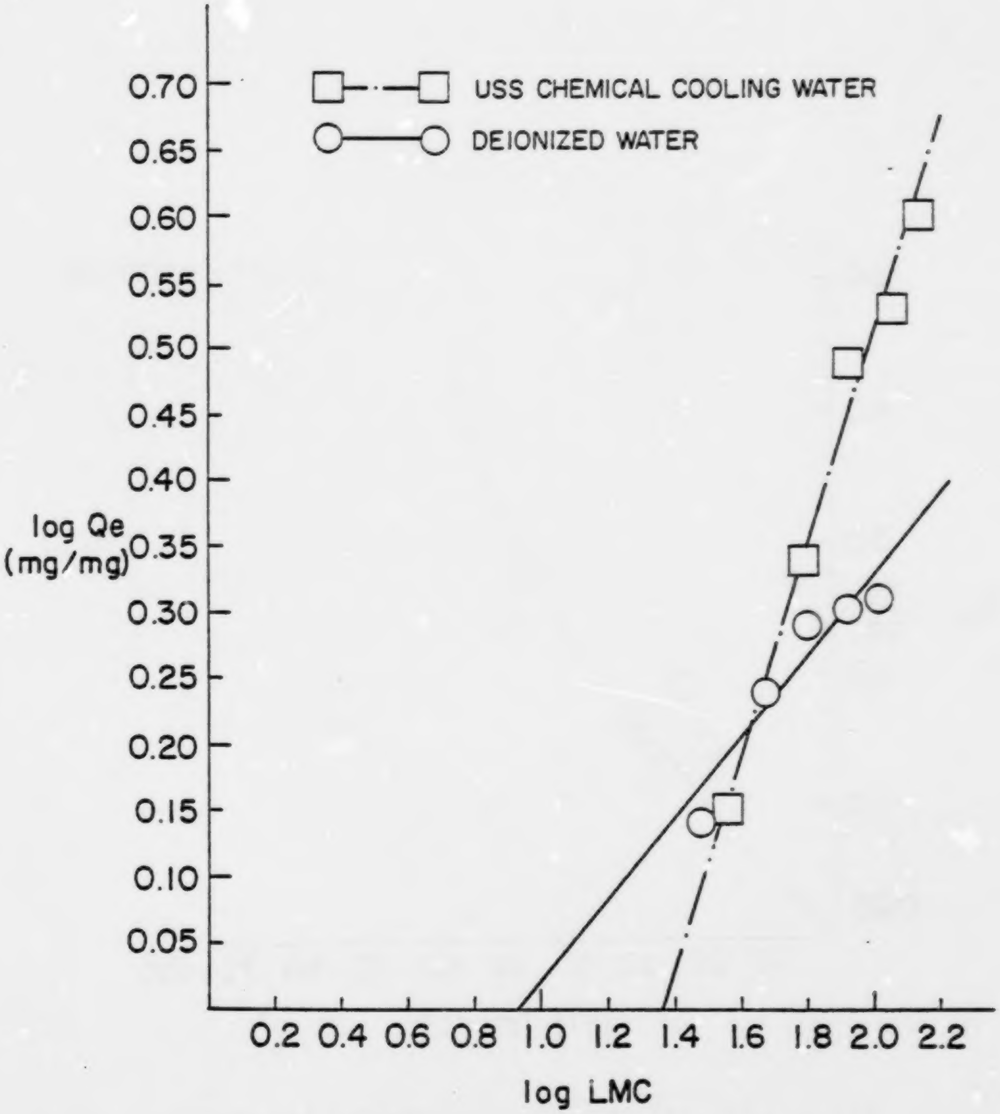


Figure 4-18. Linearized Knight isotherm for silica adsorption (Jar Tests).

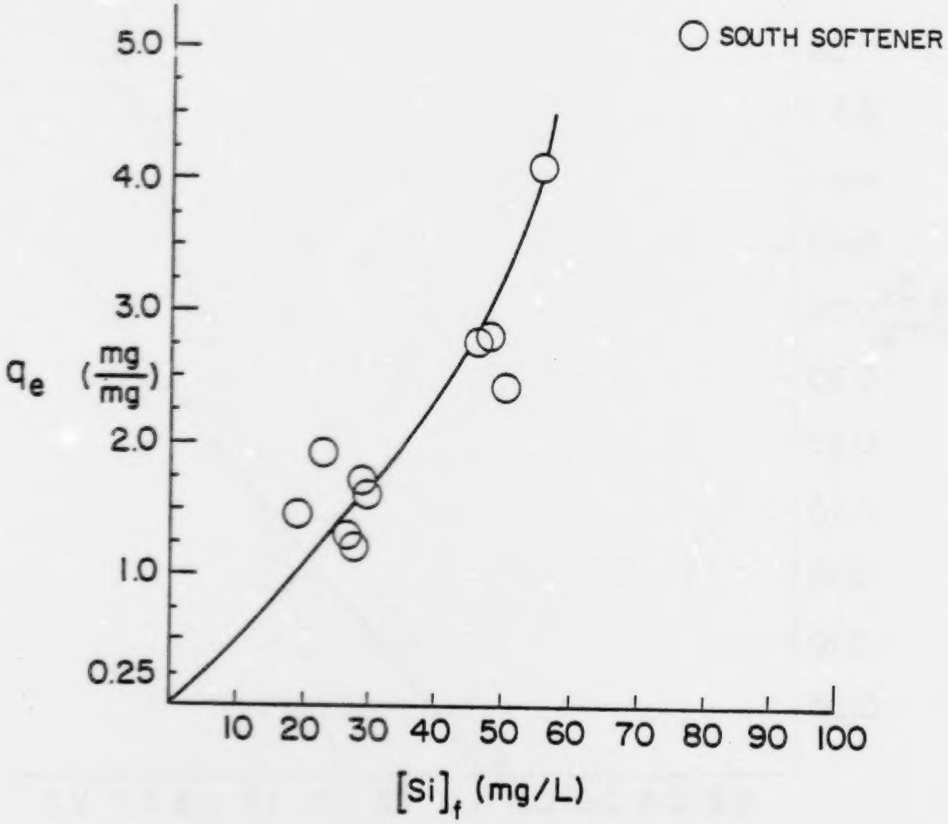


Figure 4-19. Equilibrium isotherm for adsorption of silica onto magnesium hydroxide floc (USS Chemicals south softener).

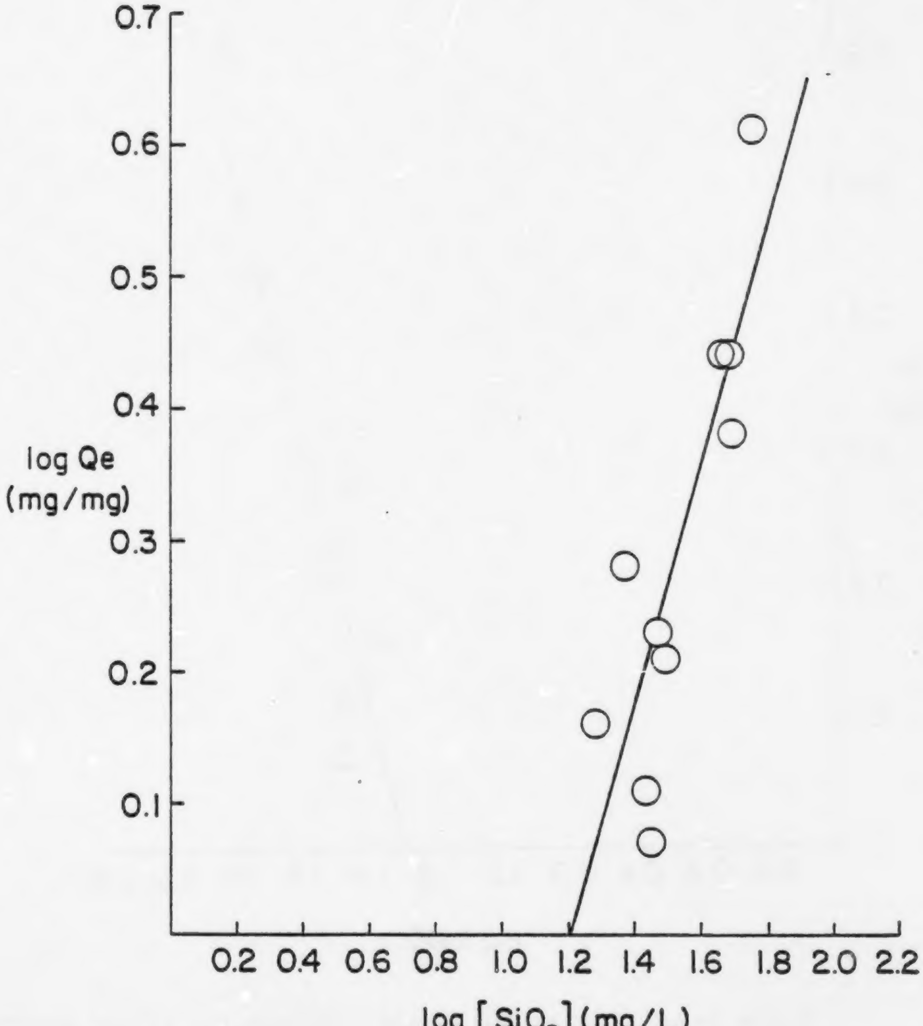


Figure 4-20. Linearized Freundlich isotherm for silica adsorption (south softener).

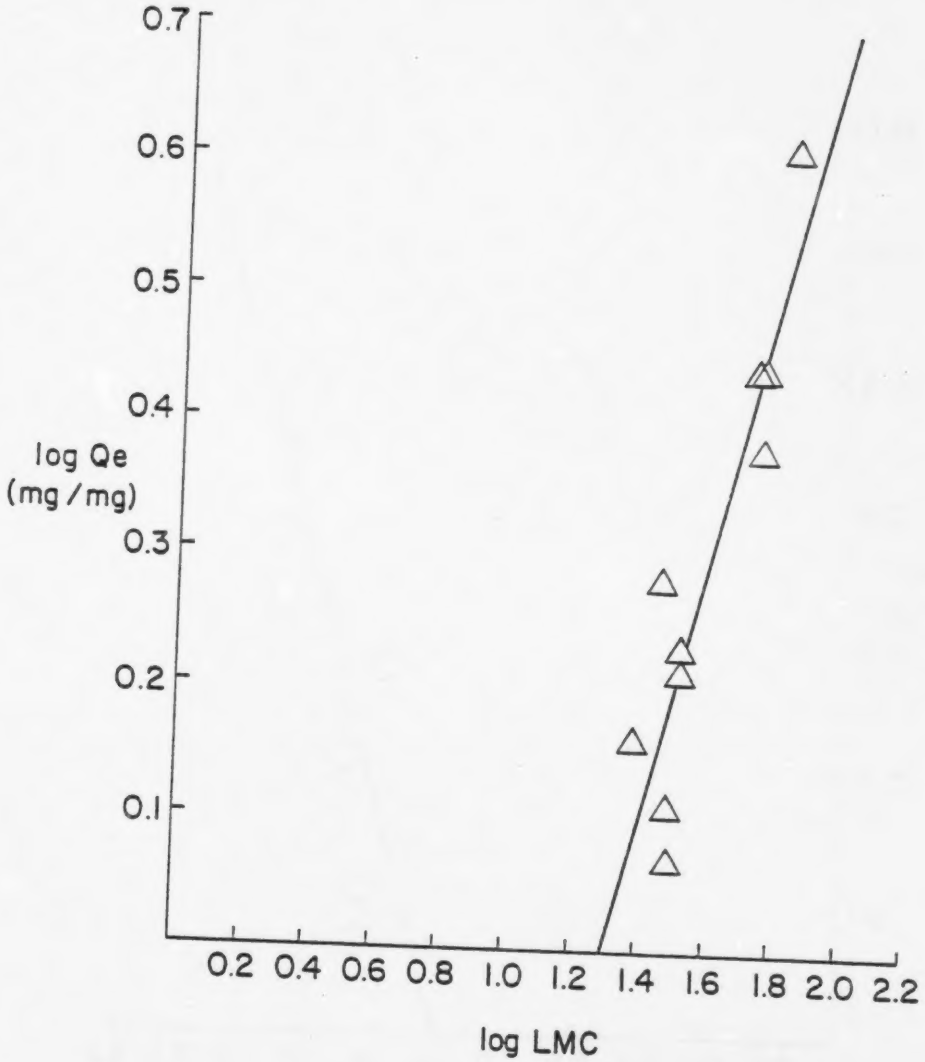


Figure 4-21. Linearized Knight isotherm for silica adsorption (south softener).

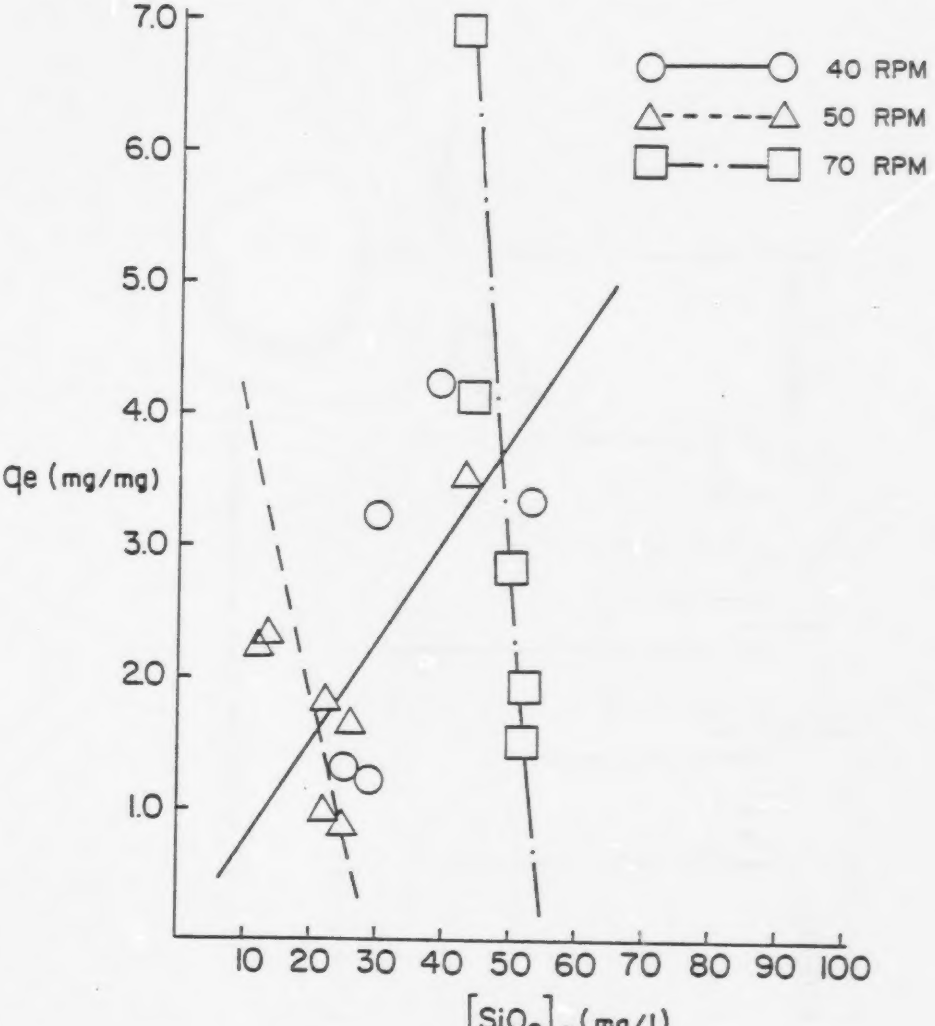
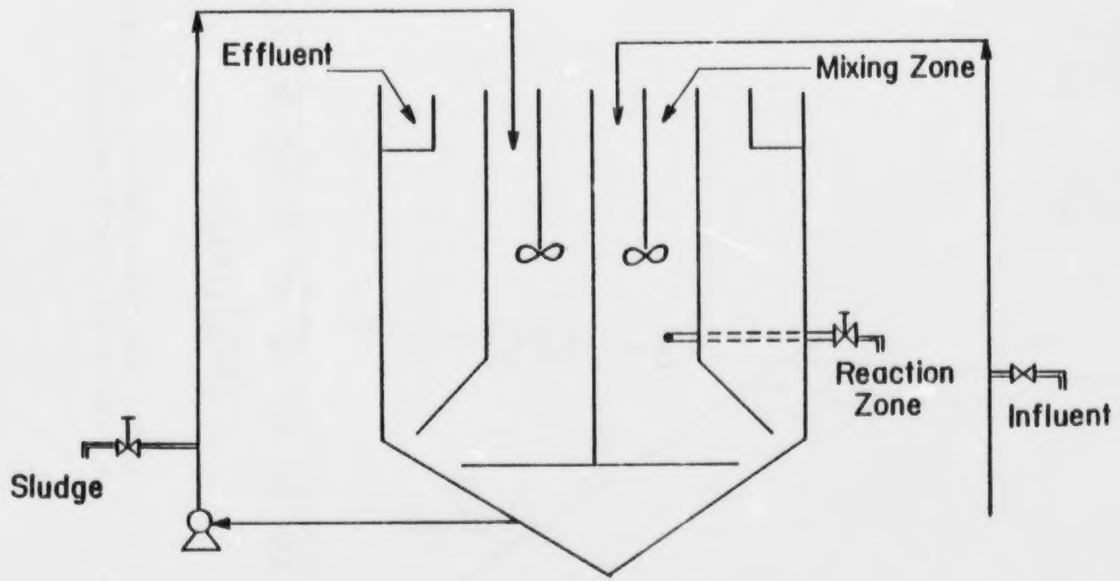


Figure 4-22. Silica adsorption iostherms obtained at various mixing speeds (north softener).


Effluent
Mixing Zone
Reaction Zone
Influent
Sludge

Schematic of Sampling Points in North Softener.

Figure 4-23.

RESULTS AND DISCUSSION

In order to analyze the efficiency of the better mixed North Softener, the data collected during the third period of the work plan was used to plot the effect of different mixing speeds on various operational parameters. For most of the cases, the shapes of the graphs were determined by the averages of several data points, since data was generally well-scattered. However, for the sake of accuracy, all data points are plotted on certain figures, and the averaged values are distinguished from the raw data presented.

Effect of Mixing Speed on Solubility Product of Calcium Carbonate

The solubility product of calcium carbonate, K_{sp}, was calculated for each grab sample according to the following calculations:

$$P.Alk = 1/2\ (CO_3^{=}) + (SiO_2) * \frac{50}{60} + (OH^-)^{**} \qquad \text{all terms as mg/L } CaCO_3$$

$$[CO_3^{=}]^* = 2(P.Alk - SiO_2 * \frac{50}{60}) * 10^{-5} \qquad \text{moles/liter } CO_3^{=}$$

$$[Ca^{2+}] = Ca^{2+}\ \text{mg/L } CaCO_3 * 10^{-5} \qquad \text{moles/liter } Ca^{2+}$$

$$K_{sp} = [Ca^{2+}][CO_3^{=}]$$

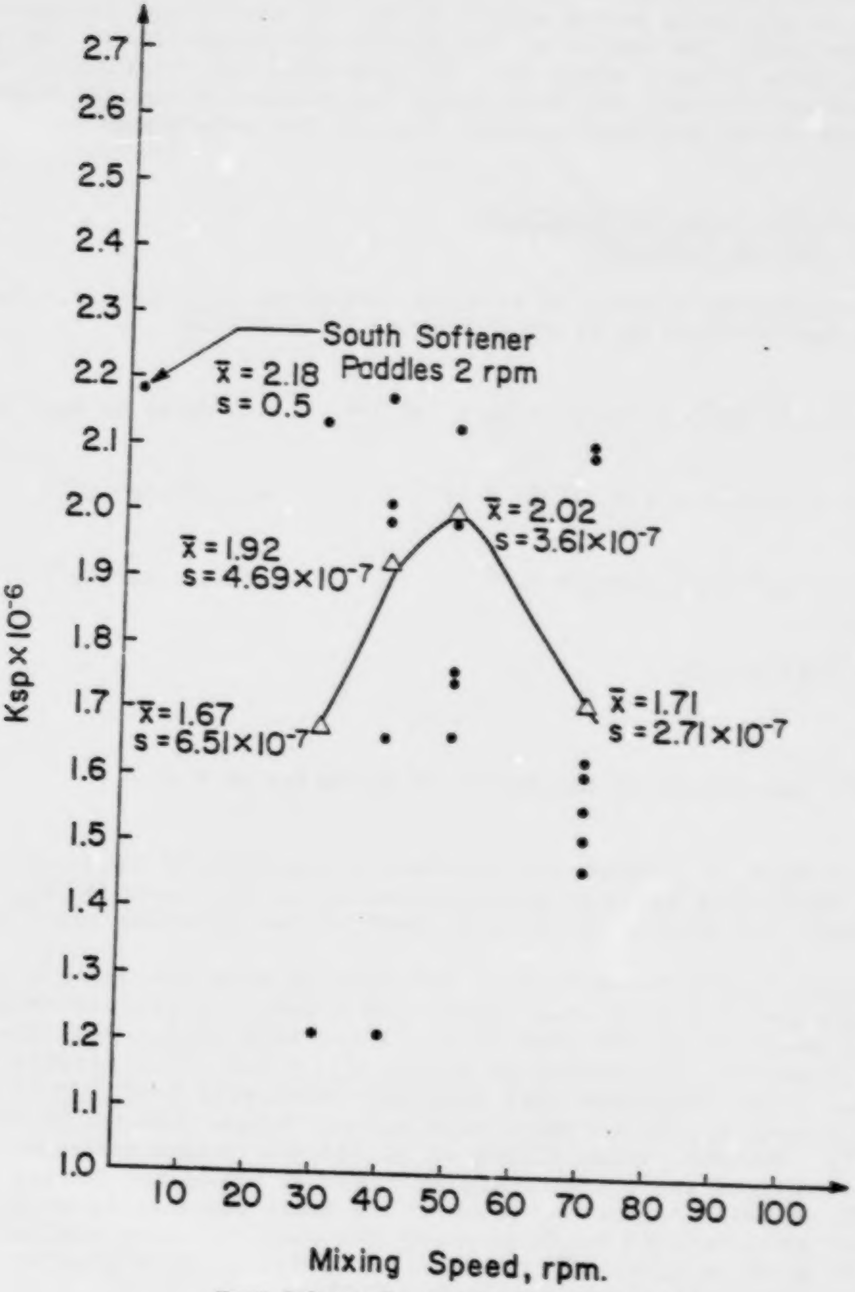
**$[OH^-]$ was considered negligible at operating pH = 10.4

When the product of calcium and carbonate concentrations in solution exceed the K_{sp}, $CaCO_3$ will begin to precipitate; hence the lower the K_{sp} value in the softener, the greater is the efficiency of the softening reaction.

Solubility products of calcium carbonate in solutions mixed at different rpm are plotted in Figure 4-26. Since the solubility product obtained for solutions mixed at speeds from 30 to 70 rpm were higher than the typical solubility product of calcium carbonate ($K_{sp} = 2.8*10^{-9}$), results indicate that in all cases solutions were supersaturated with $CaCO_3$. It is observed that the lowest K_{sp} values were obtained at 30 rpm ($1.67*10^{-6}$) and 70 rpm ($1.71*10^{-6}$). However, since mixing at 30 rpm was judged inadequate, 70 rpm may be considered the optimum mixing speed at which the lowest K_{sp} will occur. By comparison, the K_{sp} value of the South Softener in which the only motion in the reaction zone is given by the slow velocity paddles (2 rpm), the K_{sp} is equal to 2.18×10^{-6}, indicating a substantially greater tendency for calcium and carbonate to remain in solution.

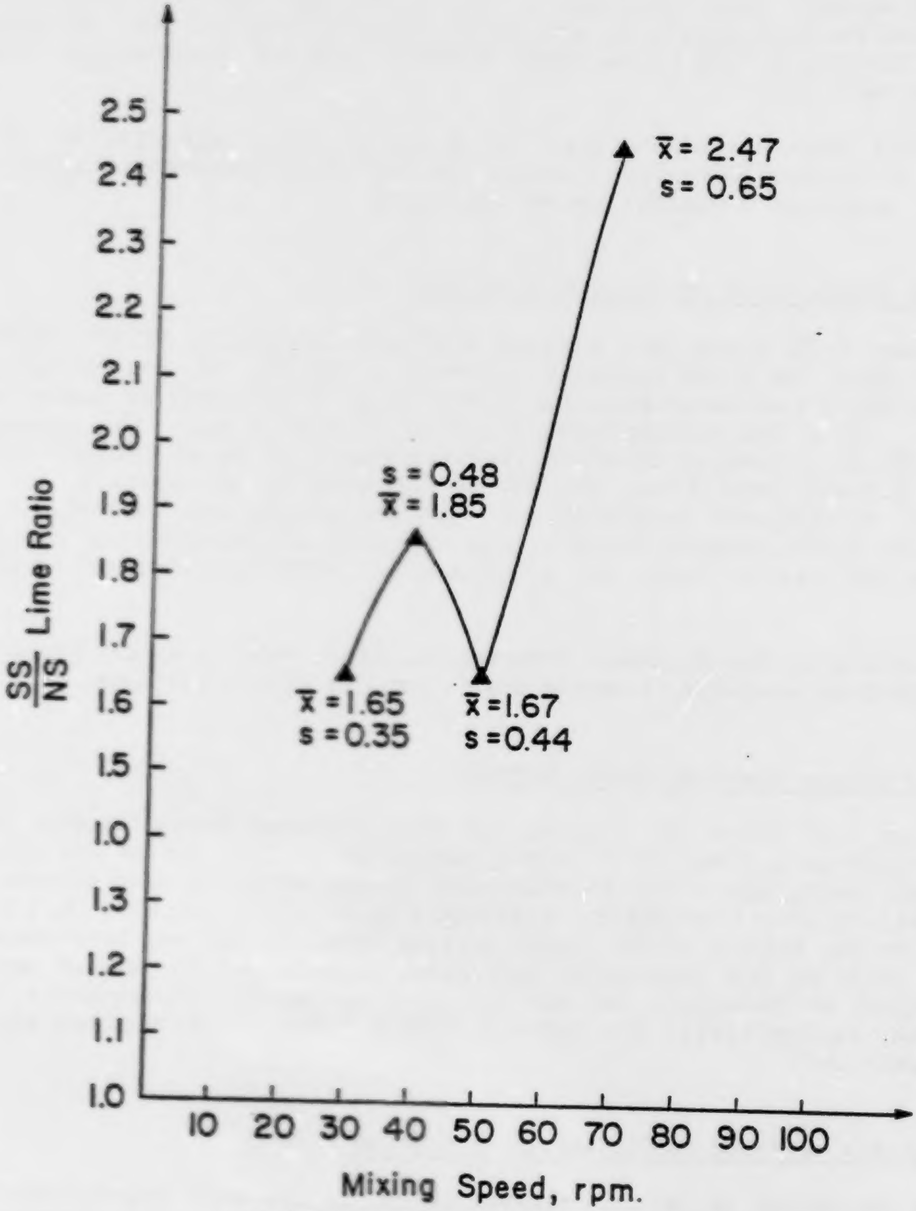
Effects of Mixing Speed on Lime Requirements

Figure 4-27 is a plot of the North Softener mxing speed versus the South



North Softener K_{sp} versus Mixing Speed.

Figure 4-24. Effect of mixing speed on calcium carbonate solubility in USS Chemicals north softener.



South Softener/North Softener Lime Ratio versus Mixing Speed in North Softener.

Figure 4-25. Effect of mixing speed on softener lime dosage.

Softener/North Softener lime ratio. This ratio compares lime requirements for the South Softener to that of the faster mixed North Softener; a higher SS/NS lime ratio indicates that less lime dosage was added to the North Softener to obtain similar softening. Accordingly, 70 rpm is the optimum mixing speed at which lime requirement in the North Softener was reduced to the least amount. This phenomena is due to the fact that high mixing helps to dissolve the lime particles, improving the softening process. By comparison, the minimum mixing in the South Softener does not dissolve the lime in the water very well.

It has been estimated that the North Softener operated at 70 rpm requires 45 percent less lime to accomplish softening comparable to the South Softener, which had a minimum amount of mixing.

Effect of Mixing Speed on Effluent Turbidity

Figure 4-28 shows the average effluent turbidity in NTU units of effluent from the North Softener operated at 30, 40, 50, and 70 rpm. the results, which indicated minimum turbidity at 40 rpm, may be explained as follows: (1) at low mixing speed (between 30 and 40 rpm), the process of nucleation or formation of new crystals occurs; (2) at 40 rpm, a hindered settling process takes place, and due to the settling of crystals, the turbidity of the effluent decreases; (3) when the mixing speed exceeds 40 rpm, the higher speeds tend to break up the crystals and create tiny particles which do not settle well, and which are not efficiently removed by the filters.

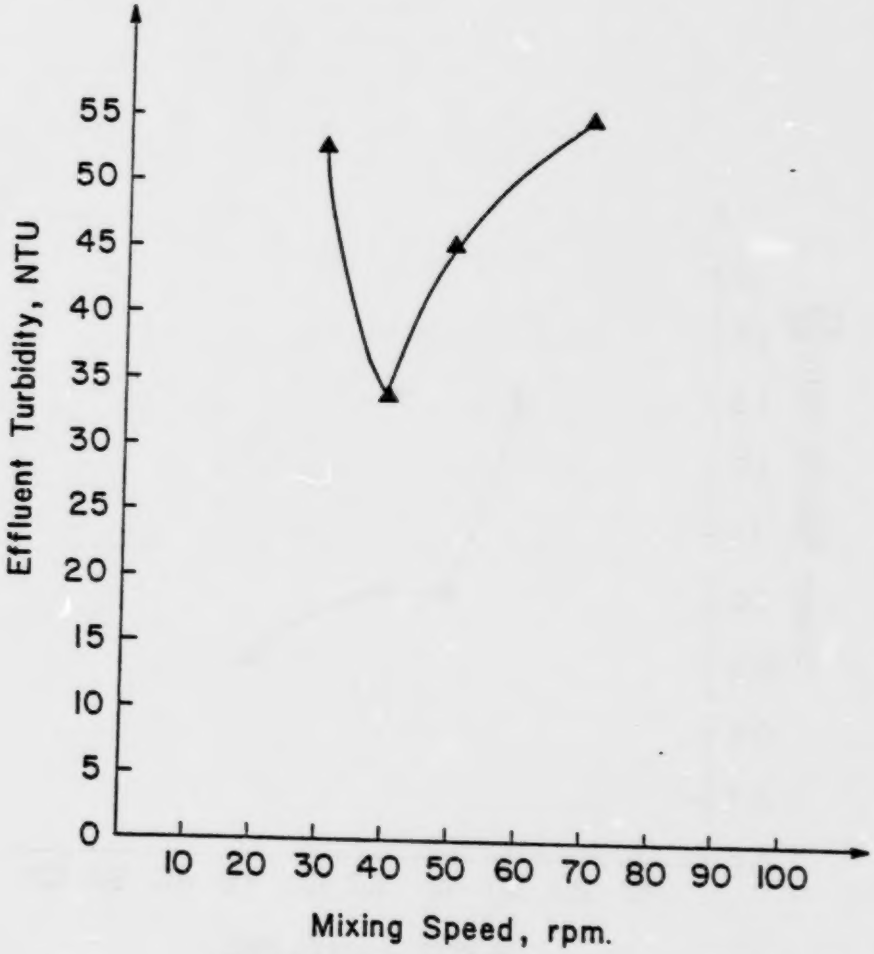
According to the phenomena observed in Figure 4-28, a mixing speed of 40 rpm is the most adequate to obtain less turbidity in the effluent.

Effect of Mixing Speed on Sludge Recycle

Figure 4-29 shows the data for the South Softener/North Softener sludge recycle rates as a function of mixing speed (rpm). Similar to the previous SS/NS lime ratio, the sludge recycle ratio in the softeners also depends upon the intensity of mixing speed. Although Figure 4-29 indicates that 30 rpm results in the highest SS/NS sludge recycle rate, it was not considered the optimum point in this particular experiment because, as was stated earlier, mixing speed is inadequate for the equipment operation. Consequently, 40 to 50 rpm may be considered the optimum mixing speed to accomplish minimum sludge recycle.

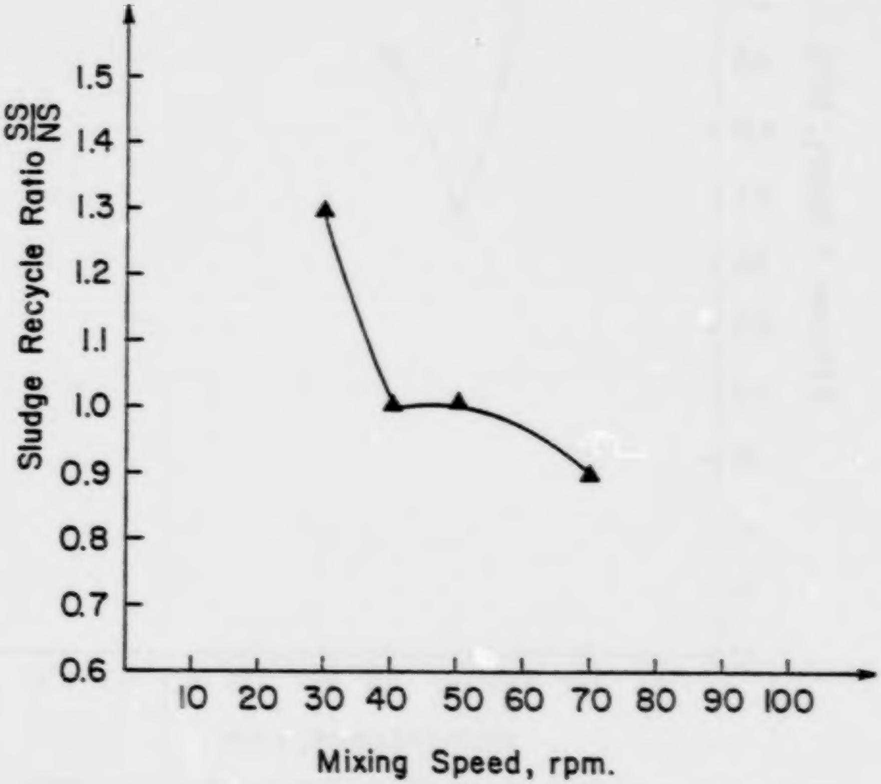
Effect of Mixing Speed on Percentage of Calcium Removal

The percentage of calcium removal is one of the most significant indicators of softener efficiency. Figure 4-30 shows a plot of percentage of calcium removal versus mixing speed. While it can be observed that the percent calcium removal was significantly improved at higher mixing speeds (as compared with the South Softener), there was no appreciable difference in removal rates among the higher speeds.



North Softener Effluent Turbidity, NTU, versus Mixing Speed, rpm.

Figure 4-26. Effect of mixing speed on softener effluent turbidity.



South Softener/North Softener Sludge Recycle Ratio versus Mixing Speed in North Softener.

Figure 4-27. Effect of mixing speed on softener sludge recycle rate.

Effect of Mixing Speed on Sludge Setting in Mixing Zone

Figure 4-31 is a plot of sludge settling in the mixing zone versus mixing speed. As can be seen from that plot, the sludge settling increased when the mixing speed increased from 30 to 50 rpm; however, less sludge setting occurred when mixing speed increased from 50 to 70 rpm. These results are comparable to those obtained for turbidity, since increased settling results in decreased turbidity. Consequently, it seems that a mixing speed of 70 rpm is preferable to producing the least sludge settling in the mixing zone.

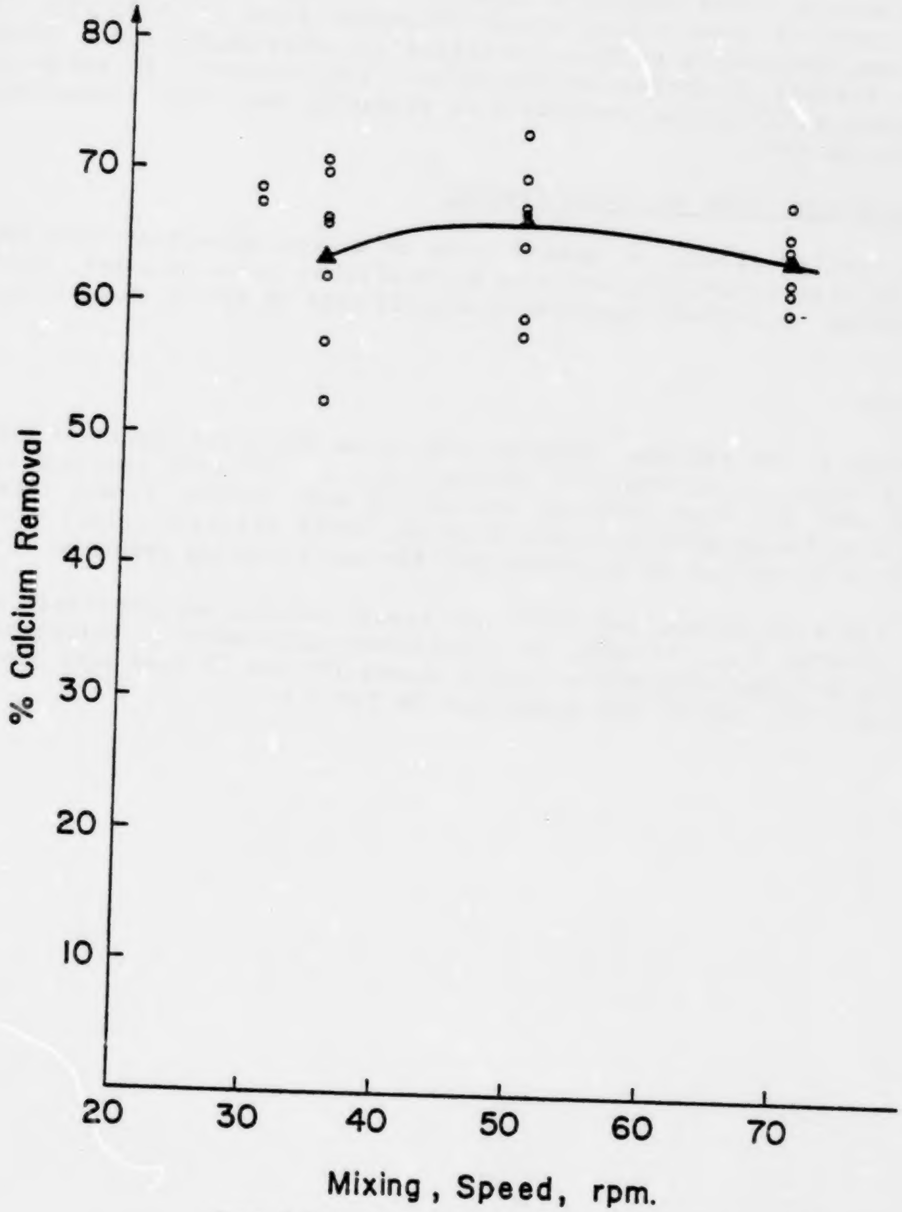
Effect of Mixing Speed on Silica Removal

The limited effects of mixing speed on silica adsorption were reported above. As stated earlier, while no quantifiable trend emerged, increased mixing seemed to increase maximum attainable rate of silica adsorption.

CONCLUSIONS

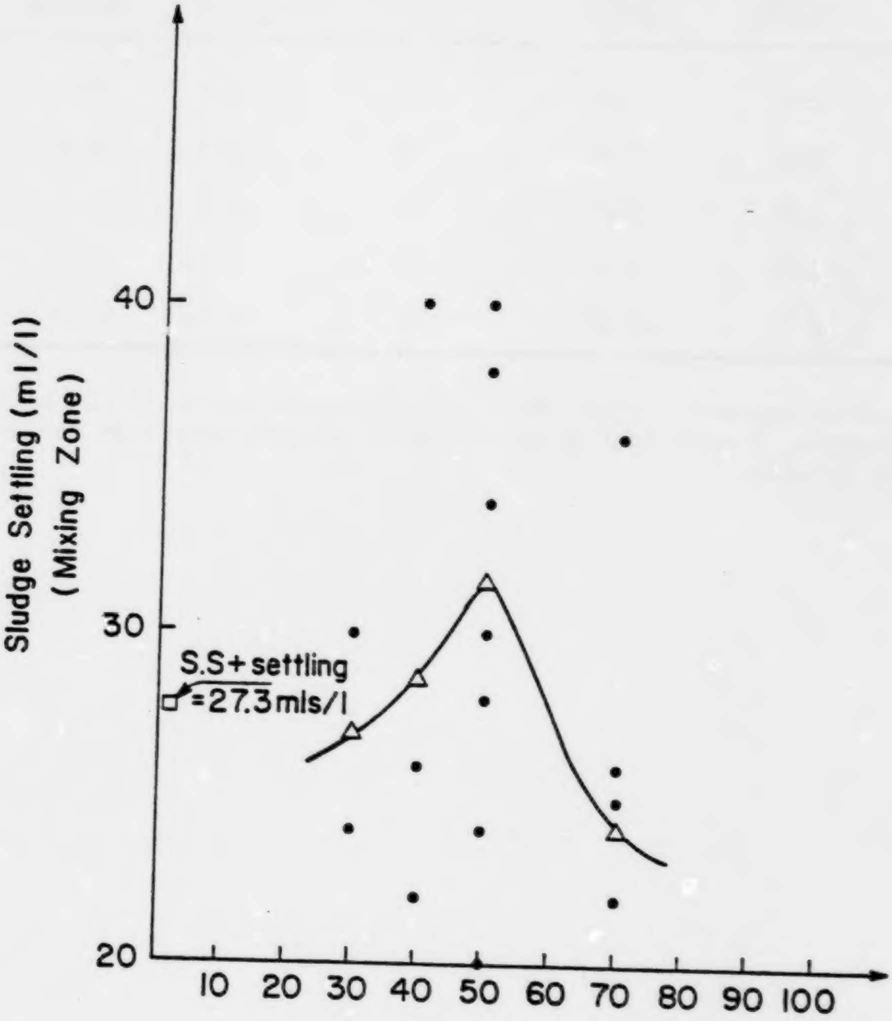
Mixing in the softener reaction zone is an important aspect of the softening process. A substantial improvement in softener performance was obtained when the North Softener was fitted with turbine mixers capable of maintaining faster mixing speeds than the South Softener. This was especially true of savings in lime required for the softening reaction.

It was also determined that once enough mixing was provided for good process control (e.g., 40 rpm), no significant difference in softening efficiency was obtained when higher mixing speeds (50 and 70 rpm) were applied to the system. The results are summarized in Table 4-7.



North Softener % Calcium Removal versus Mixing Speed, rpm.

Figure 4-28. Effect of mixing speed on calcium removal.



Sludge Settling (mixing zone, ml/L) versus Mixing Speed (rpm).

Figure 4-29. Effect of mixing speed on sludge settling in the mixing zone.

TABLE 4-7. Effect of Mixing Speed on Softener Operations

RPM	K_{sp} $(x10^6)$	Lime Ratio[†] (SS/NS)	Turbidity (NTU)	Sludge Recycle[†] (SS/NS)	Percent Ca Removed	Sludge Settling (mg/L)
2	2.18	1.00		1.0	60.9	27
30	1.67	1.65	53	1.3	68.0	27
40	1.92	1.85	32	1.0	63.4	28
50	2.02	1.67	45	1.02	65.4	31
70	1.71	2.47	55	0.90	63.5	24

[†] Indicates the ratio of the SS (South Softener) to the NS (North Softener). For example, a ratio of 1.65 means that 69 percent more lime was used in the South Softener.

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SECTION 5

MONITORING AND CONTROL OF BIOFOULING IN A ZERO DISCHARGE SIDESTREAM SOFTENED COOLING SYSTEM

Recirculating cooling tower systems (RCT) that contain high concentrations of organic matter present significant challenges to control of biofouling. Organic concentrations in cooling water are increasing because environmental regulations and higher water costs are stimulating recycle schemes involving cooling water systems. An RCT in a plant that reuses much of its process water as makeup, and also treats and reuses its blowdown will have high organic concentrations that will stimulate biofouling.

USS Chemicals, Houston, Texas, began operating a recycle/reuse RCT system in 1979. Effluent streams, including stormwater, process wastewater, and boiler blowdown, were added as makeup to the RCT system. The only effluent streams not reused were the demineralizer regeneration and rinse waters. Blowdown was treated in a lime softener for calcium, magnesium, and silica removal and recycled to the RCT system.

However, biofouling was such a problem that by January, 1981, production was limited by the resulting loss of heat transfer. Organic levels, in terms of total organic carbon (TOC), had increased to approximately 500 mg/L. In contrast, most RCT systems rarely rise above 50 mg TOC/L. Conventional biofouling control methods were not effective so a different approach was attempted in which a brominated biocide ws used in conjunction with a more traditional chlorinated control.

MATERIALS AND METHODS

To determine the effectiveness of the various biocidal treatments, a fouling monitor system* was installed on a slipstream from the cooling water return line to monitor biofouling. Its purpose was to simulate conditions in the main system and provide a real time readout of the extent of biofouling as measured by reduction in heat transfer.

In the plant control room, surface condenser vacuum was monitored. Although influenced by a variety of factors, the vacuum reading was sensitive to biofouling, and rapid decreases in vacuum (in the absence of other causes) were directly attributable to biofouling.

The total halogen residual in the cooling water was measured six times per day by the DPD colorimetric method [3]. The TOC was analyzed daily. Microorganism counts in the cooling water were also conducted on a daily basis.

The Fouling Monitor System

The fouling monitor system consisted of two major components:

1. A 0.0127 m (0.5 in) I.D. carbon steel tube containing ports (for pressure drop measurement) and a heat transfer section (consisting of an electrically heated block which was clamped around the tube). (Figures 5-1 and 5-2)

2. A microcomputer to calculate frictional resistance and overall heat transfer coefficient.

Temperature probes inserted in the heated block determined the radial temperature profile; the system also included a flow meter and bulk water temperature probes. Both the pressure drop and entrance length sections were heated to match surface temperature conditions in the heat transfer section. Output from the microcomputer was displayed on a television monitor and included all pertinent measurements and calculations. A cassette recorder stored the data. The system is diagrammed in Figure 5-3.

To simulate a composite heat exchanger in the plant, the fouling monitor was operated at the following conditions.

1) Flow rate was maintained at 0.90 m s^{-1} (3 fps) by constant head feed tank with a manually controlled valve;

2) Feed water temperature was maintained at 40°C by a manually controlled heat exchanger; and

3) Electric power to the block was maintained at 100 watts

Data was averaged over each hour of operation and recorded on an hourly basis. Output consisted of the parameters listed in Table 5-1.

Data and calculations were recorded on cassette tape and transcribed at a later date. Manual determinations of temperatures and pressure drop were conducted approximately every three days as a check of computer results and to anticipate a computer failure. Bulk water and block temperature were measured manually using a Yellow Springs Instrument Tele-Thermometer and pressure drop was measured with an inclined mercury manometer.

Overall Heat Transfer Coefficient

Overall heat transfer coefficient is defined by

$$U = \frac{q}{2Lr_{ii}\ (T_2 - TB)}$$

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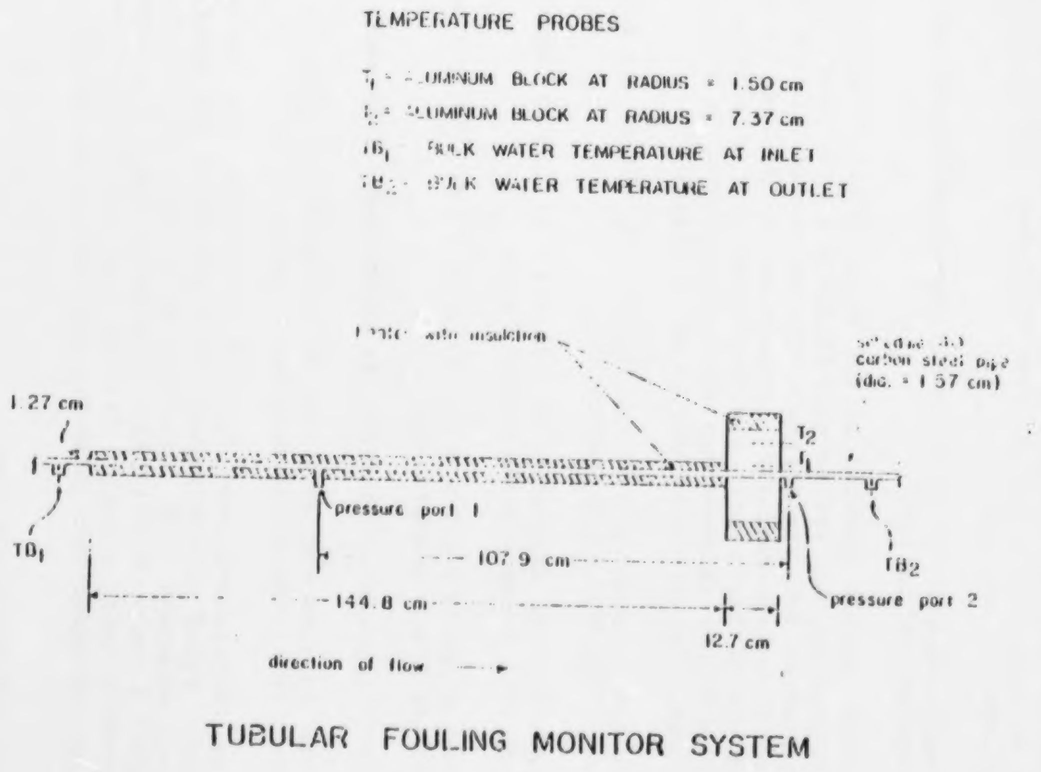
TEMPERATURE PROBES
T_1 = ALUMINUM BLOCK AT RADIUS = 1.50 cm
T_2 = ALUMINUM BLOCK AT RADIUS = 7.37 cm
TB_1 = BULK WATER TEMPERATURE AT INLET
TB_2 = BULK WATER TEMPERATURE AT OUTLET
with insulation
carbon steel pipe
(dia. = 1.57 cm)
1.27 cm
T_2
T_1
TB_1
pressure port 1
107.9 cm
TB_2
144.8 cm
pressure port 2
12.7 cm
direction of flow
TUBULAR FOULING MONITOR SYSTEM

Figure 5-1. Apparatus for monitoring biofouling in the USS Chemicals cooling system.

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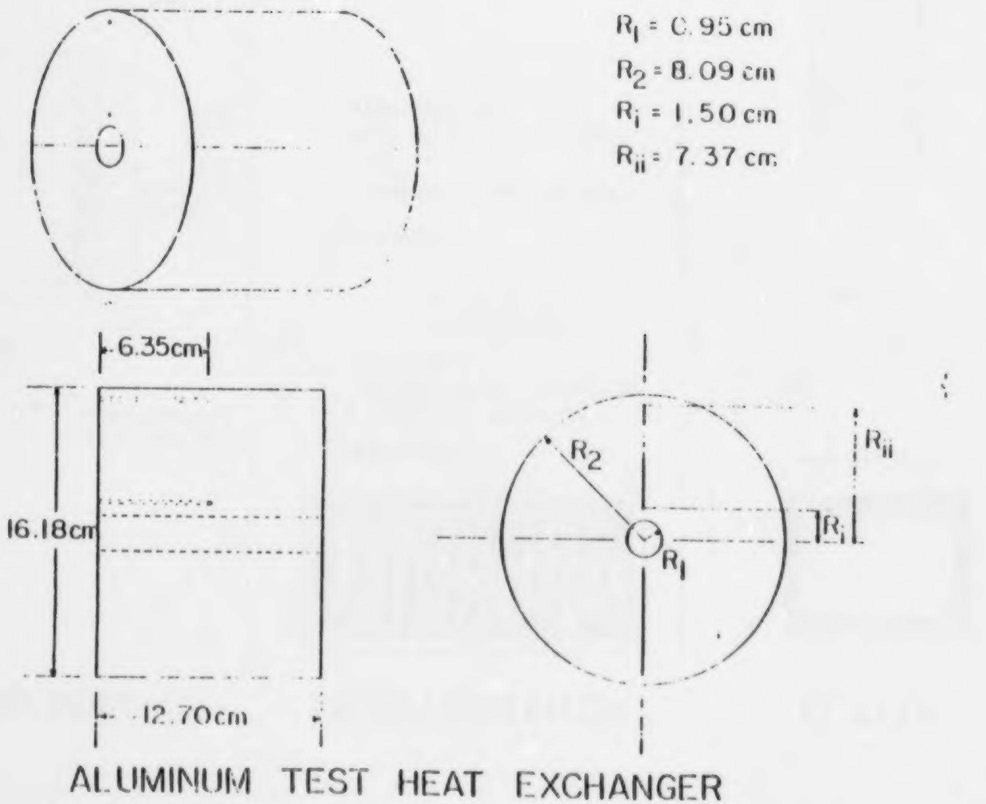
R_I = C.95 cm
R_2 = 8.09 cm
R_i = 1.50 cm
R_{ii} = 7.37 cm
6.35cm
16.18cm
12.70cm
R_2
R_I
R_i
R_{ii}
ALUMINUM TEST HEAT EXCHANGER

Figure 5-2. Detail of biofouling monitor apparatus showing aluminum heat exchanger.

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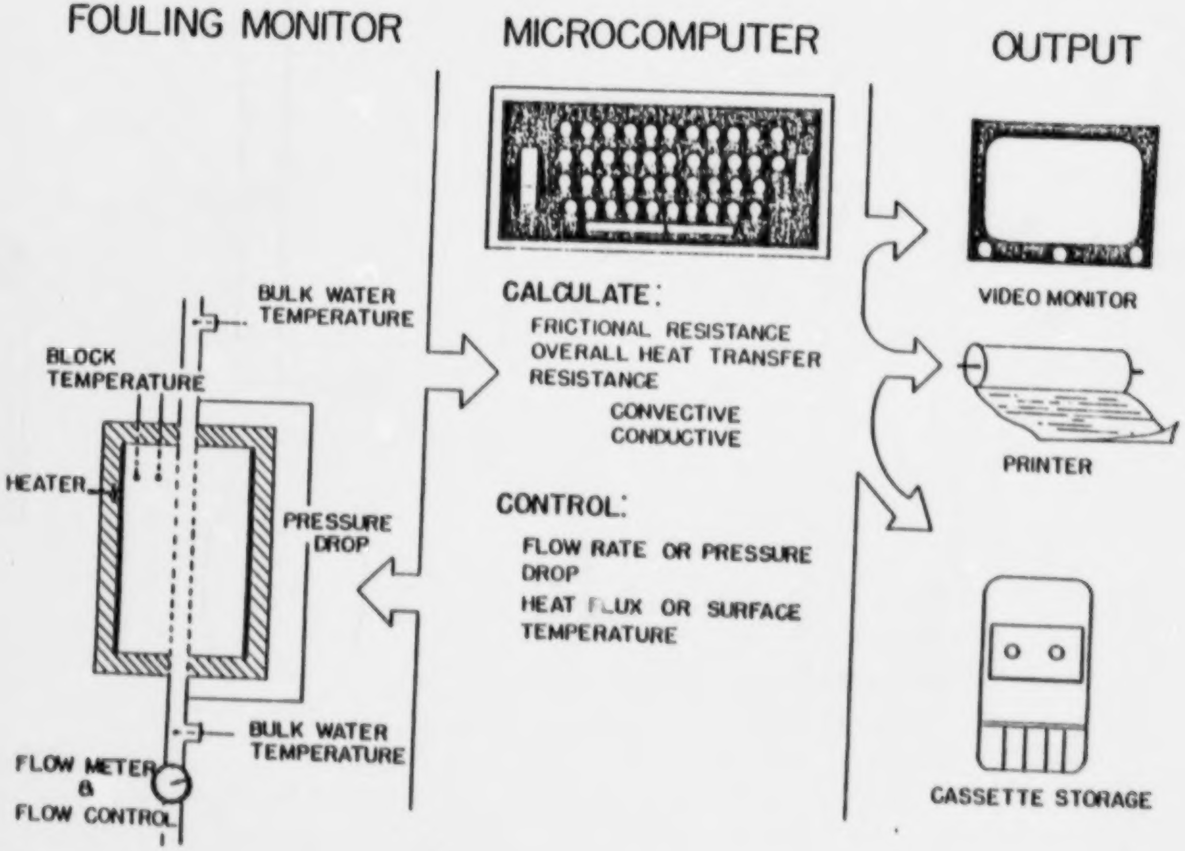

FOULING MONITOR
MICROCOMPUTER
OUTPUT
BULK WATER TEMPERATURE
BLOCK TEMPERATURE
HEATER
PRESSURE DROP
BULK WATER TEMPERATURE
FLOW METER & FLOW CONTROL
CALCULATE:
FRICTIONAL RESISTANCE
OVERALL HEAT TRANSFER RESISTANCE
CONVECTIVE
CONDUCTIVE
CONTROL:
FLOW RATE OR PRESSURE DROP
HEAT FLUX OR SURFACE TEMPERATURE
VIDEO MONITOR
PRINTER
CASSETTE STORAGE

Fouling Monitor System

Figure 5-3. Process diagram of biofouling monitor system.

TABLE 5-1. The Output of Fouling Monitor/Microcomputer System

FOULING MONITOR MEASUREMENTS	MICROCOMPUTER CALCULATIONS
-Bulk water temperature at the tube inlet, TB1	-Overall heat transfer coefficient, U, using a heat flux calculated from the thermal conductivity of the block and the difference between T_1 and T_2
-Bulk water temperature at the tube outlet, TB2	
-Block temperature at two radii, T1, T2	-Friction factor, f, from pressure drop and flow rate data
-Flow rate, F	
-Pressure drop, Δp	

TABLE 5-2. Abbreviations and Symbols

NOTATION	UNITS
d = tube diameter	(m)
f = friction factor	(dimensionless)
F = flow rate	(ms^{-1})
g = gravity	(ms^{-2})
k = thermal conductivity of block	$(Wm^{-1}{}^{o}C^{-1})$
L = length of heat transfer section	(m)
L_p = length between pressure ports	(m)
q = applied heat	(W)
r_i = block radius at 0.0150 m	(m)
r_{ii} = block radius at 0.0737 m	(m)
T_1 = block temperature at r_i	(^oC)
T_2 = block tempertaure at r_{ii}	(^oC)
TB = average bulk water temperature	(^oC)
TB_1 = bulk water temperature at the tube inlet	(^oC)
TB_2 = bulk water temperature at the tube outlet	(^oC)
U = overall heat transfer coefficient	$(W\ m^{-2}{}^{o}C^{-1})$
U^{-1} = overall heat transfer resistance	$(W^{-1}m^{2}{}^{o}C)$
v_m = mean fluid velocity	$(m\ s^{-1})$
Ap = pressure drop	(m Hg)
ρ_f = fluid density (water)	$(kg\ m^{-3})$
ρ_{Hg} = density of mercury	$(kg\ m^{-3})$

Overall heat transfer resistance, U^{-1}, is the inverse of U. The heat flux, q, was maintained constant and was calculated from T_2 and T_1 and the thermal conductivity of the heated block.

$$q = \frac{2\ L\ k\ (T_2 - T_1)}{\ln\ (r_{ii}/r_i)}$$

Frictional Resistance

Frictional resistance is characterized by the dimensionless friction factor.

$$f = \frac{2\ d\ \Delta p\ \rho_{Hg}\ g}{L_p\ \rho_f\ v_m^2}$$

where ρ_{Hg} is the specific gravity of mercury, ρ_f is the fluid specific gravity, L_p is the pressure drop length, and v_m is linear mean velocity (see Table 5-2 for an explanation of symbols and

Sampling Method and Analytical Techniques for Deposit Characterization

Two 0.05 m length sections of tubing, in series with and identical to the heat transer section tubing, were removed with a pipe cutter; one tube was preserved in a 100 mg/L $HgCl_2$ solution to prevent biological growth and the other stored in a dry container.

The preserved sample tube was analyzed for total mass by removing the attached mass and drying for three hours at 103°C. The sample was cut in longitudinal sections to observe pitting and corrosion and stored, with dessicant, for comparison with later samples.

The bacterial count was determined by removing the biomass with a rubber policeman, diluting to 25 mL and then performing a standard plate count [1]. The areal bacterial density was determined by dividing the total number of bacteria on the sample tube by the inside area of the tube. The standard plate count does not permit development of the more fastidious aerobes or obligated anaerobes and other potentially important aquatic bacteria.

Identification of bacteria was performed by observing morphological characteristics of different colonies (i.e., gram stain, cell size, motility, and endospores) and by observing cultural characteristics of macroscopic appearance on growth media (i.e., amount of growth, color, opacity, and form). Further identification was made using indole, oxidase, citrate, glucose, and catalase tests. The standard MPN procedure [1] was used to determine presence of coliform bacteria.

Control Strategy

The chemicals originally used for biofouling control were chlorine, a surfactant, and a non-oxidizing biocide. Chlorine was added continuously to the RCT by bubbling the gas through the water in the cooling tower basin. Free chlorine residual levels were maintained in the 0.05 - 0.2 mg/L range. The surfactant (chlorine helper) was also added continuously. The non-oxidizing biocide (a quaternary amine) was batch fed to the system three times per week. In response to excursions in which heat transfer was reduced, additive rates were increased to maximum levels.

The alternative control strategy was the use of Bromocide®, (bromochlorodimethylhydantoin, or BCDMH) manufactured by Great Lakes Chemicals, as a complement to gaseous chlorine. Gaseous chlorine mixes with water to produce hypochlorous acid according to the following reaction:

$$Cl_2 + H_2O \rightleftharpoons HOCl + H^+$$

The product, hypochlorous acid, in turn establishes an equilibrium with the hypochlorite ions

$$HOCl \rightleftharpoons OCl^- + H^+$$

as described by the equation

$$K_1 = \frac{[H^+][OCl^-]}{[HOCl]}$$

The pK of the reaction, which equals 7.5 at low ionic strength and temperatures of 20°C, decreases at higher ionic strengths and temperatures. In the cooling water at USS Chemicals, the pK approaches 7.0 at a temperature of 30°C and ionic strength of 0.5. Thus, the predominant species is the hypochlorite ion.

However, the hypochlorite ion is a much stronger oxidizing agent than hypochlorous acid, and dissipates quickly with organic material. More importantly, the hypochlorite ion is a less effective biocide because the microorganisms can more easily repel the charged ions. Conversely, the uncharged hypochlorous acid can diffuse readily into a microbial cell [2].

Bromocide® was chosen as an alternative to gaseous chlorine since it is a more effective biocide in the pH range encountered at USS Chemicals. (7.6 - 7.8). Bromine chemistry is analogous to chlorine chemistry in that the bromine will form hypobromous acid and hypobromite ion. Moreover, the pK is approximately one pH unit higher than chlorine, i.e., $pK_1 = 8.63$ [3]. Therefore, the predominant species of bromine in the USS Chemicals cooling water is hypobromous acid.

RESULTS AND DISCUSSION

Debugging of the biofouling monitor system was completed in late 1980. In January, 1981, the comprehensive monitoring system commenced operation, including analysis of halogen residual, viable cell counts, and measurement of condenser vacuum was in operation.

Before Bromination

During the first thirty days, the condition of the cooling water deteriorated as shown in Figure 5-4, which indicates that the surface condenser vacuum decreased from a high of 25 inches of mercury to a rough average of 21. (A decrease in vacuum indicated intensified biofouling.) In an attempt to counteract the biofouling, increased amounts of chlorine were added to the cooling water system. As shown in Figure 5-5, the free residual rose to an average of 0.5, but the biofouling condition persisted.

Section of heat exchanger tubing was wthdrawn on January 24 (Figure 6). The fouling deposit was concentrated on the bottom of the tube. Corrosion and pitting was evident on the tube surface after the deposit was removed.

Dry mass of the fouling deposit (103°C for 3 hours) was 32.38 g cm^{-2}. A bacteria count revealed approximately 380 organisms per cm^2 of the tube wall surface. The bacterial count was conducted several days after the sample was removed and should be considered as an estimate.

Preliminary investigation of types of bacteria revealed the presence of *Actinomycetes*, *Bacillus*, *Flavobacterium*, *Moraxella*, and *Alcaligenes*. No coliform organisms were present.

After Bromination

On day thirty, the chlorinators were shut down and the BCDMH was added to the system at a rate of 100-150 lbs/day. The results of the BCDMH addition are shown in Figure 5-6, which indicates the reduction of fouling by the change in heat transfer resistance and frictional resistance, respectively, in the fouling monitor. Heat transfer resistance increases steadily due to fouling, up to approximately day ten (actually day 30 of the test). After that, heat transfer resistance decreases to approximately clean conditions. The decrease in heat transfer resistance begins immediately after the change to BCDMH treatment.

Figure 5-6 also indicates the progression of friction factor. The results are almost identical to heat transfer resistance. Friction factor increased steadily until BCDMH was added, then the friction factor decreased to clean conditions.

For the next thirty-day period, BCDMH was added with the surfactant and non-oxidizing biocide. As Figure 5-4 shows, the condenser vacuum gradually increased into the range of 23 to 24 inches of mercury; there was also visual

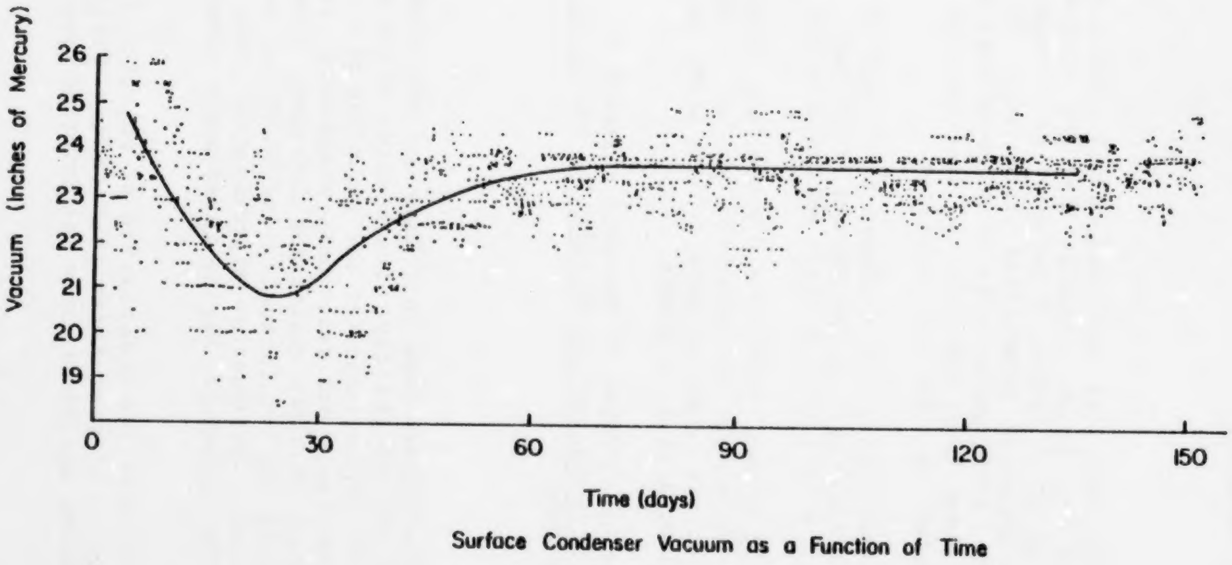
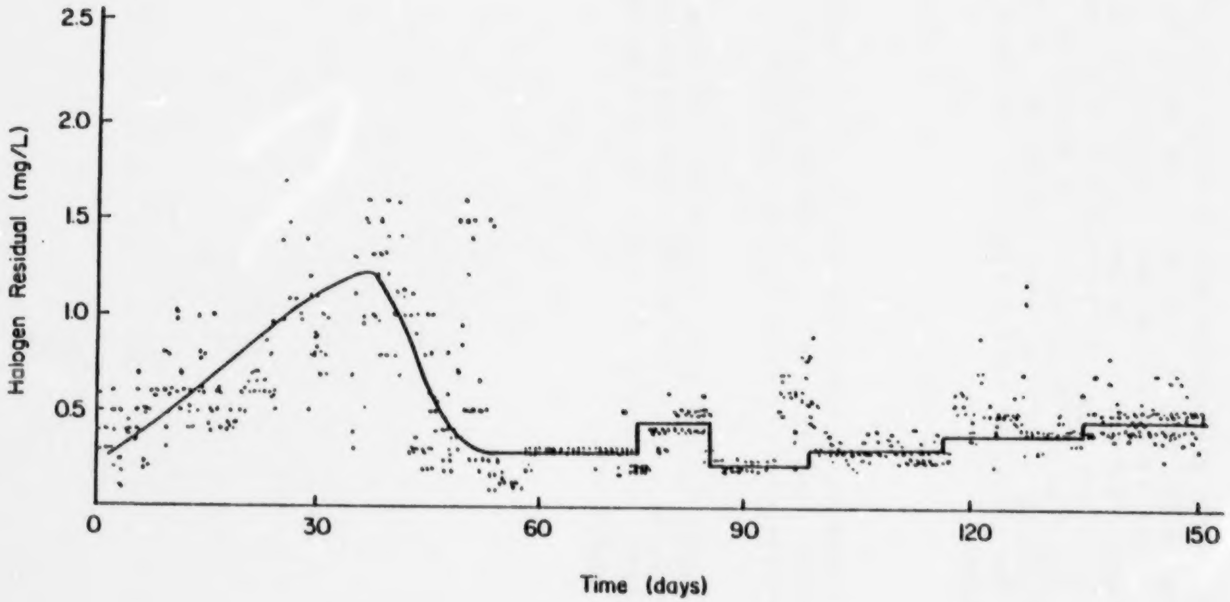


Figure 5-4. Variations in surface condensor vacuum of the biofouling monitor apparatus.



Free Halogen Residual for Recirculating Cooling Water as a Function of Time

Figure 5-5. Variations in cooling water free halogen residual.

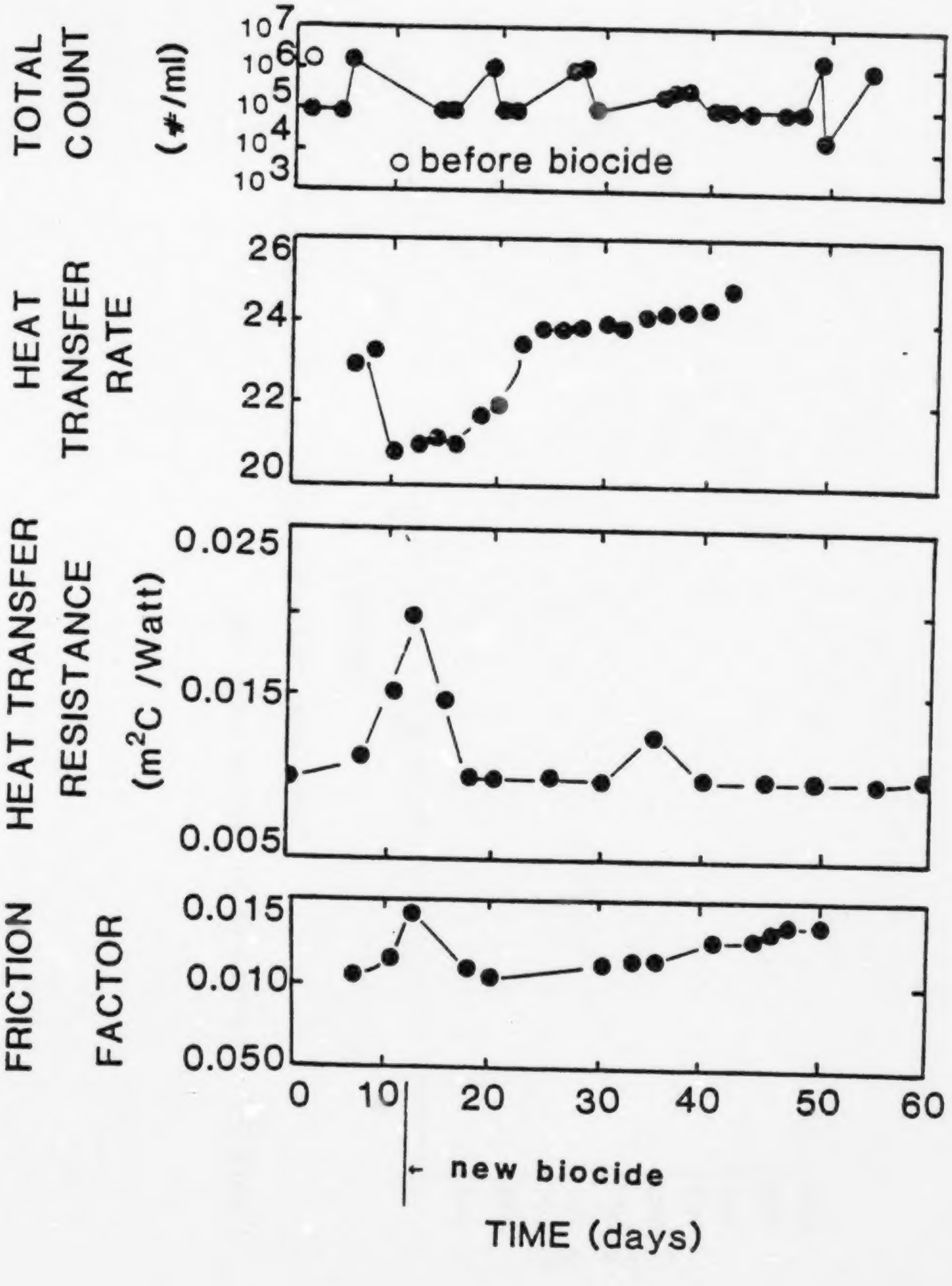
evidence of biofilm reduction. Stringers on the cooling tower slats gradually disappeared. The TOC and viable cell count measurements were not indicative of biofouling conditions in the cooling water system. The TOC actually increased during the month of February as shown in Figure 5-7. However, the increase may have been an artifact of the cleanup operation rather than evidence of higher organic loadings to the system. The viable cell counts showed no sensitivity to biofouling or the resultant cleanup operation, as shown in Figure 5-8.

Starting at day ninety, BCDMH was blended with chlorine on a 1:10 weight ratio basis which was roughly 30 lbs:300 lbs/day to decrease the cost of biofouling control. The cooling water system was considered to be in good condition. Over the next ninety-day period, an operational strategy evolved in which the free halogen level was gradually increased by step changes from 0.25 to 0.45 at 0.05 mg/L intervals. The goal was to establish minimum residual level at which biofuling incidences were negligible. At 0.45 mg/L, this level was achieved. The condenser vacuum gradually increased and stabilized at an acceptable level.

CONCLUSIONS

The bromine compound BCDMH was effective in the control of biofouling in a high pH, high organic content cooling water. In conjunction with chlorine, it produced a free halogen residual which proved an effective strategy in biofouling control.

Furthermore, the biofouling monitor was a sensitive, real time indicator of biofouling. While condenser vacuum was a key plant parameter for the detection of biofouling, viable cell counts and total organic carbon did not correlate with biofouling conditions.



Heat Transfer Resistance and Friction Factor as a Function of Time

Figure 5-6. Variations in friction and heat transfer resistance as indications of fluctuations in biofouling

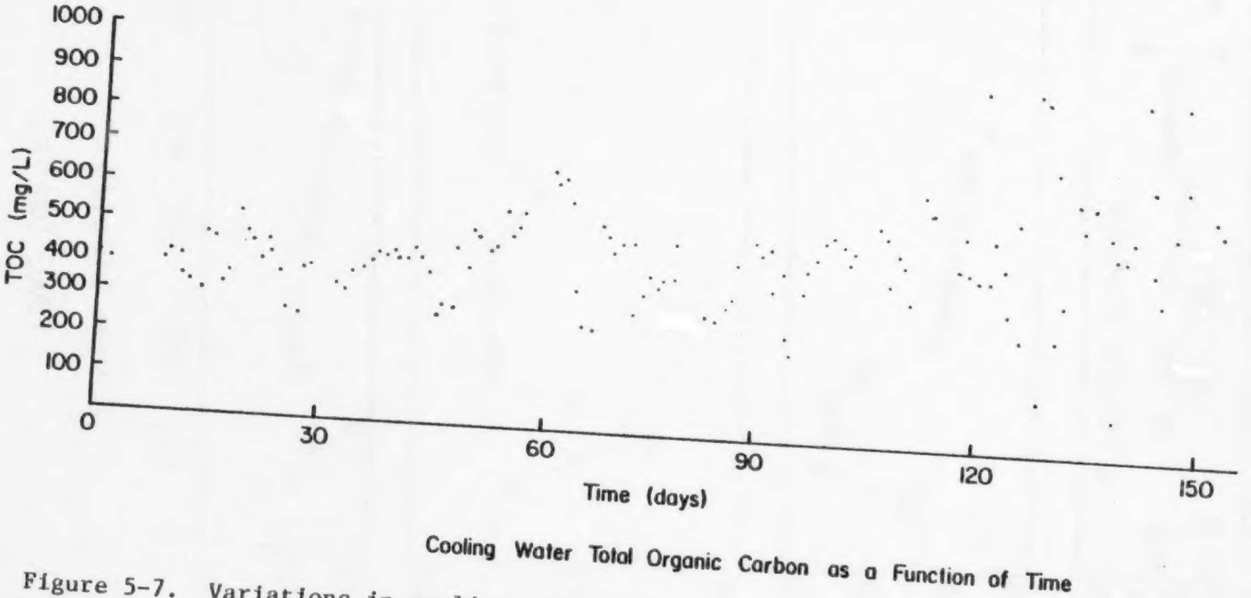
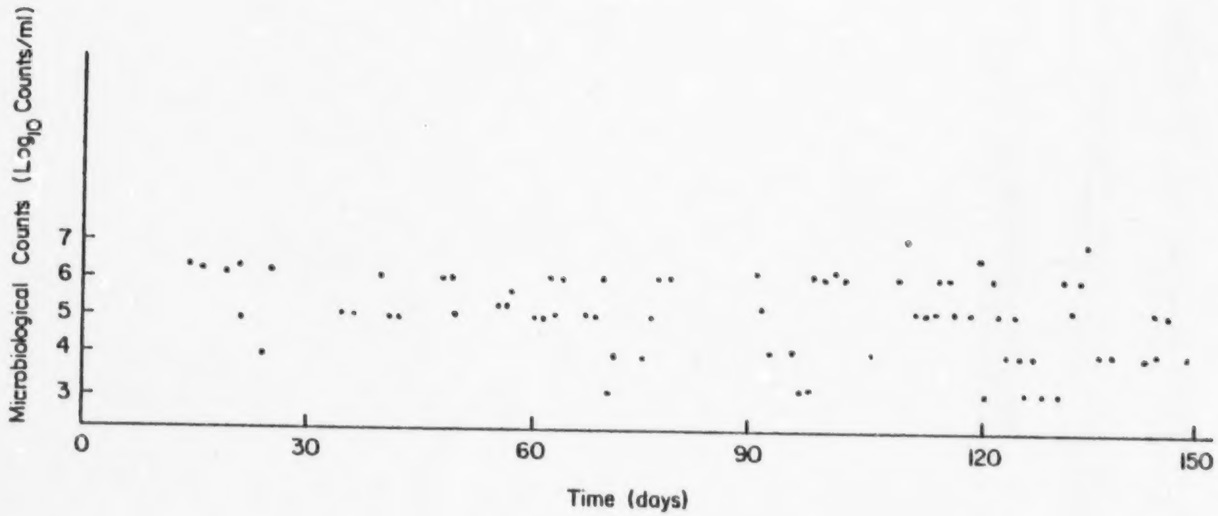


Figure 5-7. Variations in cooling water TOC.



Cooling Water Viable Microbial Cell Counts as a Function of Time

Figure 5-8. Variations in viable microbial cell counts in USS Chemicals cooling water.

SECTION 5 - REFERENCES

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SECTION 6

TREATMENT OF CHROMATE IN SOFTENER SLUDGE AND COOLING TOWER BLOWDOWN

Of all the substances used routinely in the sidestream-softened zero-discharge cooling system, chromate is the most toxic and the most problematic in terms of its ultimate disposal. Chromate is added to cooling water in the hexavalent form (Cr(VI)) which is also the most toxic. Although Cr(VI) is not removed by the softening reaction, some portion of soluble chromate (perhaps as Cr(III)) does in fact precipitate into the softener sludge with calcium carbonate and magnesium hydroxide. Careful evaluation of softener sludge for chromium leachate potential can determine the extent of landfill containment required for proper disposal of chromate-bearing sludge. Furthermore, in the event that blowdown of chromate-treated cooling water is required, chromate may be successfully removed by precipitation with ferrous sulfate ($FeSO_4$) prior to discharge.

EVALUATION AND HANDLING OF CHROMATE LEACHATE FROM SOFTENER SLUDGE

Disposal of chromate-bearing sludge from the sidestream softener is regulated by state and federal waste disposal authorities, including the US Environmental Protection Agency (EPA) and, in the state of Texas, the Texas Department of Water Resources (TDWR). This report deals primarily with the toxicity tests specified by those agencies, which determine both the extent to which chromate-bearing sludge is hazardous, and whether it must be placed in a permitted, secure, hazardous landfill , or a non-hazardous landfill.

In 1976, the Resource Conservation and Recovery Act (RCRA) was passed by Congress, and in May, 1980, Subtitle C of the Solid Waste Act was amended by RCRA "...to promulgate regulations to protect human health and the environment from improper management of hazardous waste..." Subtitle C of RCRA also established a federal program which, when fully implemented, will provide "cradle-to-grave" regulation of hazardous waste. Although parts 261-265 of RCRA collectively contain the first phase of EPA's regulations carrying out these directives, this report concerns only subpart C ("Characteristics of Hazardous Waste") Section 261.24 ("Characteristics of EP Toxicity"), and Appendix II ("EP Toxicity Test Procedure"). The current maximum concentration of chromium allowable in non-hazardous leachate is one hundred times the National Interim Primary Drinking Water Standard of 0.05 mg/L, or 5.0 mg Cr/L leachate by the EP toxicity test.

Also in 1976, TDWR issued a series of nine technical guides dealing with industrial solid waste management. These technical guides defined wastes according to their physical and chemical characteristics, and offered criteria for the selection and siting of treatment alternatives, including ponds and lagoons, landfarms, and landfills. In addition, they specified the necessary monitoring and recordkeeping systems required by state law for continuous handling of hazardous waste. The current TDWR maximum chromium concentration allowable in leachate is the same as the federal standard, 5.0 mg Cr/L leachate, as determined, however, by the Texas toxicity test.

The EPA regulations, RCRA, and the TDWR guidelines were promulgated in response to the alarming proliferation of non-authorized and unsuitable landfills across the country, and were designed to stem the serious health hazards they pose. In contrast, the new federal and state regulations require compacted clay liners for many types of landfills, and outline proper handling procedures (including complete manifests) for all hazardous waste. Also, these regulations specify tests to determine the hazard posed by a given material, and its suitability for disposal in a properly maintained landfill.

MATERIALS AND METHODS

One such candidate for landfill disposal is the sludge from the softener at the USS Chemicals plant. The thickened sludge is composed primarily of precipitated $CaCO_3$, $Mg(OH)_2$ and some $Cr(OH)_3$, and is vacuum-filtered to a final thickness of 75-80 percent solids. In appearance, it is a firm, light brown cake which dries to a fine powder.

The lime-softened sludge used in testing was collected in a plastic bag which was placed directly underneath the vacuum filter. A representative sample was collected from the entire width of the filter by moving the bag back and forth underneath the point of discharge. The bag was then sealed so as to prevent the passage of moisture in or out of the sludge. A sample of the sludge was weighed in the laboratory, dried at 105°C for at least 24 hours, then weighed again to determine the percent solids. The sludge was divided into two parts, one part to be used for each of the leachate tests investigated.

EP Toxicity Test

The EP toxicity test was performed as follows:

1. 100 g sludge (wet weight) of particle diameter   9.5 mm was placed in a stainless steel extractor (Associated American instruments) along with deionized water equal to sixteen times the sludge weight, or 1600 mL.

2. The extractor was agitated with a two-bladed impeller, and the initial pH was measured.

3. Since pH was greater than 5.0 (± 0.2), it was adjusted with 0.5 N acetic acid at a maximum rate of 4.0 mL/g sludge, or 400 mL

4. The extractor was agitated for a specified period of time, after which the mixture was raised to a final volume equal to twenty times the initial sludge weight, according to the formula

$$V = 20w - (16w + A)$$

where

V = volume of deionized water

w = weight of initial sludge sample

16w = volume of deionized water previously added in step (1)

A = volume of acid added in step (5)

After the sludge mixture was brought to the proper final volume, it was decanted and filtered through a 0.45 um Millipore filter, and the filtrate was analyzed for chromium. As a regulatory test, the EP toxicity test is run for 24 hours, but for experimental purposes, it was performed six different times from 3 to 30 hours in duration, with duplicate samples run for each time period tested.

Texas Toxicity Test

The Texas toxicity test, based on the dry weight of the sludge sample, was performed as follows:

1. After percent solids measurements were made, a wet sludge sample with an equivalent dry weight of 250 g was placed in a 2000 mL Erlenmeyer flask with 1 L deionized water.

2. The solution was stirred for five minutes, stoppered, and allowed to settle for a specified period of time.

Following the settling period, the solution was decanted and filtered through a 0.45 m Millipore filter, and the filtrate was analyzed for chromium. As a regulatory test, the Texas toxicity test is run for seven days, but for experimental purposes, it was performed for five different times from one to nine days, with duplicate samples for each duration. EP and Texas toxicity tests are compared in Table 6-1.

In addition to the toxicity tests performed, further investiations were made into the rate of chromium adsorption onto the previously leached sludge. These tests were performed with the sludge sample leached for seven days according to the Texas toxicity test method. This sludge sample was divided into three portions of 20 g each which were in turn exposed for one hour to 150 mL of deionized water containing 20, 40, and 60 mg Cr/L, as described in Figure 6-1. Sludge samples containing reabsorbed chromium were then leached

TABLE 6-1. Comparison of Extraction Procedures

TDWR	EPA
Distilled Water Leaching Medium	Acetic Acid Leaching Medium
7 days	24 hours
250 g sample + 1000 L DI water	Wet sample + 16x its weight in DI water
	Lowering pH to 5 ± 0.2 with acetic acid
Represents a more realistic eluant to be used in tests to simulate mono-landfilling operations	Increases solubility of certain trace elements while decreasing others
	Differing amounts of acid used in each case some solids will dissolve more than others
Based on dry weight	Based on wet weight

again, according to the Texas toxicity test methods, and both the leachate and the resultant sludge were tested for chromium.

Determinations of chromium in both sludge and filtrate were made according to Standard Methods. Total chromium was determined by graphite furnace atomic absorption spectrophotometry, while hexavalent chromium was determined by the colorimetric method. However, the colorimetric method was not used to determine hexavalent chromium in the EP toxicity test leachae, since addition of the diphenylcarbazide to that solution produced a white, milky precipitate instead of the normal color development. Instead, the EP leachate was raised to pH 8.0 to precipitate $Cr(OH)_3$, and the remaining solution was filtered through a 0.45 m Millipore filter, and analyzed for chromium by atomic absorption spectrophotometry. Hexavalent chromium was thus determined to the be total chromium left in solution after $Cr(OH)_3$ precipitation.

RESULTS AND DISCUSSION

Results of the Texas toxicity test, showing leachate concentration (total Cr and Cr(VI)) at various testing periods, are presented in Table 6-2, and summarized in Figure 6-2. As can be seen, Figure 6-2 indicates that relatively high concentrations of chromium are leached from the softener sludge in the first day of testing, from which point on the chromium appears to be readsorbed onto the sludge from the leachate. From an initially high leachate concentration of 1.25 mg total Cr/L, the leachate chromium concentration drops off by 40 percent over the next three days to 0.77 mg total Cr/L by the fifth day. Between days five and seven, leachate chromium concentration decreases an additional 29 percent to 0.55 mg total Cr/L, with yet another 29 percent decrease to 0.38 mg total Cr/L by the ninth day. Thus, while the leachate concentration decreases more slowly over time, leachate chromium does not appear to reach equilibrium with the sludge during the period of the experiment.

The concentration of Cr^{6+} in the sludge leachate also decreased over time. In all, the leachate Cr^{6+} concentration decreased about 60 percent in nine days, as compared to a decrease in total leachate chromium concentration of 70 percent during the same period of time. however, since the initial Cr^{6+} concentration was relatively small (0.5 mg Cr^{6+}/L), the nominal concentration of hexavalent chromium in the softener sludge leachate changed very little, indicating that in nine days the sludge/leachate mixture had more nearly reached equilibrium with respect to Cr^{6+}. Furthermore, the total chromium leachate concentration gradually approached the Cr^{6+} leachate concentration, suggesting that Cr^{3+} was removed from the leachate by readsorption onto the sludge, while the Cr^{6+} remained in solution. Thus, it might be expected that at the time of true equilibrium, the total chromate concentration in the softener sludge leachate would consist entirely of hexavalent chromium.

The significance of Cr^{3+} readsorption is also supported by the observation that total chromium in the leachate decreases as the pH drops below 8.0. According to Thomas and Theis [4], the normal range of minimum solubility for $Cr(OH)_3$ (Figure 6-3), pH 8-10, is shifted to a more acidic range in solutions

TABLE 6-2. Texas Test Leachate Values
(expressed as parts per million)

Days Run	Total Cr ppm	Cr^{6+} ppm	Cr^{3+} ppm	pH (Ave.)
1	1.25	0.50	0.75	7.9
3	0.770	0.50	0.27	7.8
5	0.785	0.465	0.29	7.8
7	0.530	0.29	0.50	7.1
9	0.380	0.205	0.19	7.0

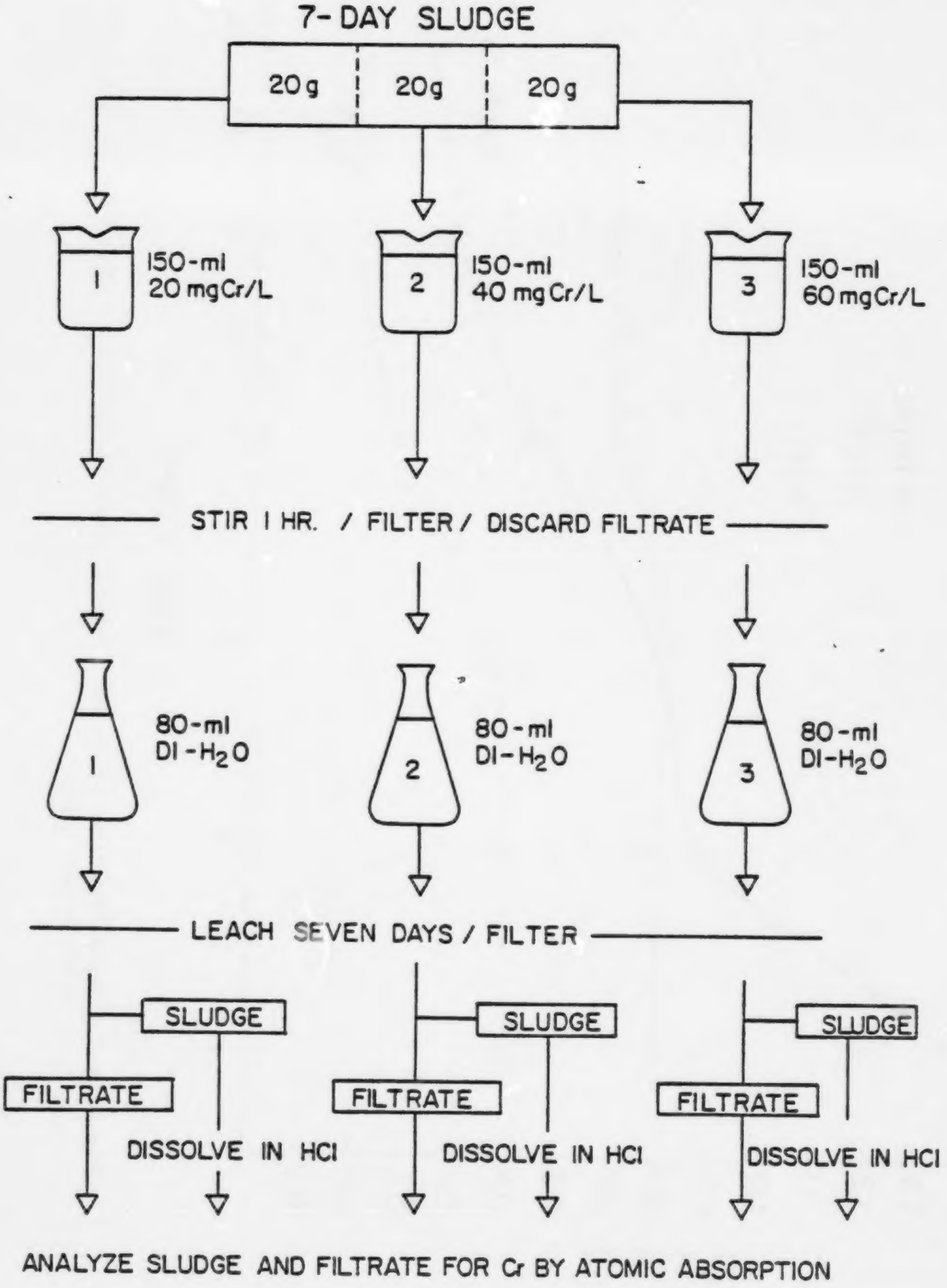

7- DAY SLUDGE
20g
20g
20g
1
150-ml
20 mgCr/L
2
150-ml
40 mg Cr/L
3
150-ml
60 mgCr/L
STIR 1 HR. / FILTER / DISCARD FILTRATE
1
80-ml
DI-H2O
2
80-ml
DI-H2O
3
80-ml
DI-H2O
LEACH SEVEN DAYS / FILTER
SLUDGE
FILTRATE
DISSOLVE IN HCl
SLUDGE
FILTRATE
DISSOLVE IN HCl
SLUDGE
FILTRATE
DISSOLVE IN HCl
ANALYZE SLUDGE AND FILTRATE FOR Cr BY ATOMIC ABSORPTION

Figure 6-1. Process diagram for leached chromate adsorption study.

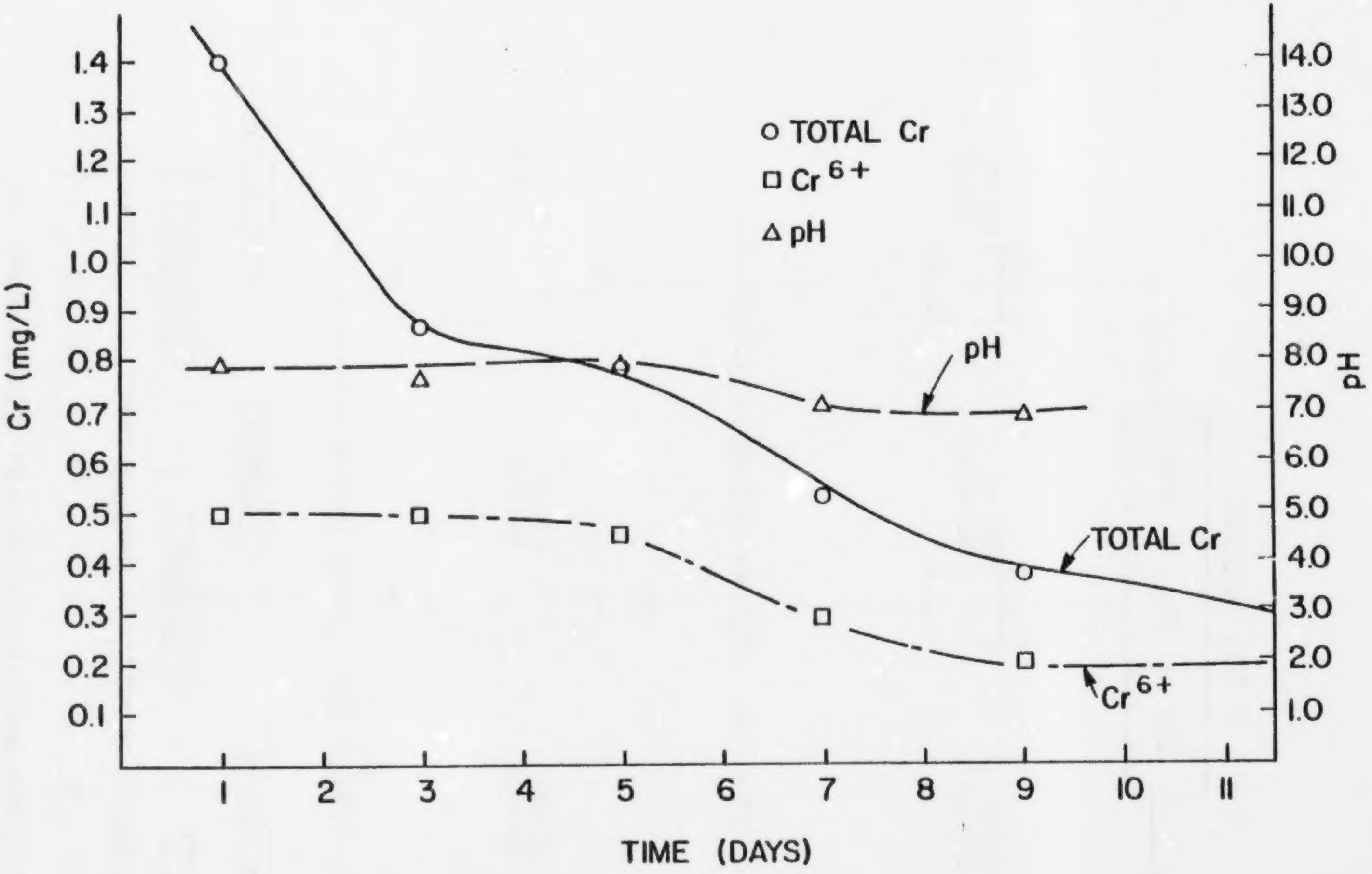
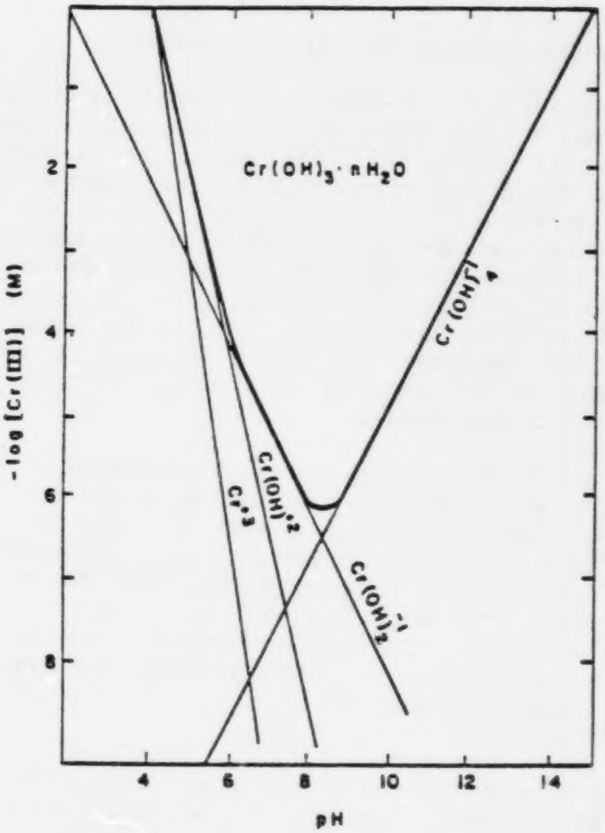


Figure 6-2. Equilibration of Texas Toxicity Test to determine chromate in softener sludge leachate.



Concentration distribution of various Cr(III) species as governed by the solubility of solid Cr(OH)$_3$·nH$_2$O.

Figure 6-3. Solubility of Cr(OH)$_3$ as a function of solution pH.

with high concentrations of carbonate. Since, at pH less than 8, most carbonate is converted to bicarbonate, it is not unreasonable to suppose that at that point also the Cr^{3+} in the sludge leachate becomes increasingly insoluble, causing the total dissolved chromium concentration in the leachate to decrease.

The EP toxicity test results (Figure 6-3) indicate a steep increase in leachate chromium during the first nine hours of exposure. However, once a high point was reached (0.38 mg total Cr/L), the chromium concentration in the leachate also began to decline, until it apparently reached an equiibrium concentration at 18 hours, which was 52 percent lower (0.185 mg total Cr/L). In contrast to this dramatic behavior, Cr^{6+} concentration appeared relatively stable, at around 0.04 mg/L, varying little throughout the duration of these test, suggesting that differences in total chromium concentration in the leachate were caused by varying concentrations of chromium(III).

The most likely explanation for the change in Cr^{3+} found in the leachate is that $Cr(OH)_3$ in the softener sludge dissolved under the acidic conditions specified in the EP toxicity test (Figure 6-3), increasing the leachate chromium concentration. However, the dissolution of $Cr(OH)_3$ also served to raise the pH of the solution, causing the Cr^{3+} to precipitate. Thus it can be seen in Figure 6-4 that the steepest decrease in leachate chromium concentration corresponded to the steepest increase in pH (from 3.8 to 6.3), which in turn corresponds to the decreasing solubility of chromium(III). The variation of Cr^{3+} concentration with pH would therefore account for both the surge and the decline of total chromium in the leachate. The slight increase in hexavalent chromium during the early hours of the test may also result from the release of chromate in the sludge upon acidification.

A comparison of the EP and Texas toxicity tests is presented in Table 6-4, for the specified duration of the tests, i.e., 24 hours for the EP test, and seven days for the Texas test. Results indicate that the EP toxicity test, which comes to equilibrium quickly under acidic conditions, shows chromium to be less easily leached from softener sludge than the more "conservative" Texas toxicity test. The Texas toxicity test, in which Cr^{6+} is determined by the diphenylcarbazide colorimetric method also indicates a greater amount of hexavalent chromium in the sludge leachate than does the EP toxicity test, which $Cr(OH)_3$ precipitation and atomic absorption for determination of hexavalent chromium.

Studies of adsorption of chromium onto softener sludge indicated a generally favorable adsorption isotherm (Figure 6-5) plotted according to the linearized Freundlich model in Figure 6-6. As mentioned earlier, adsorbed chromium was considered to be that portion which did not leach out of the sludge when exposed to deionized water for seven days; hence, the values are somewhat lower than those for total chromium adsorbed by the sludge after one hour of exposure to the various chromium solutions. In all cases, Cr^{6+} comprised a relatively constant, small percent of adsorbed chromium, on the order of 1 percent (Figure 6-7).

TABLE 6-3. EPA Leachate Values
(expressed as parts per million)

Hours	Duplicates	Total Cr	Cr^{6+}	Cr^{3+}	pH
3	1	0.210	0.0250	0.185	4.4
	2	0.240	0.0185	0.222	4.0
6	1	0.460	0.0295	0.431	4.0
	2	0.250	0.0250	0.225	3.5
12	1	0.330	0.0370	0.293	5.4
	2	0.360	0.0335	0.327	7.0
18	1	0.260	0.0350	0.225	
	2	0.110	0.0610	0.049	
24	1	0.160	0.0355	0.125	7.4
	2	0.240	0.0400		5.3
30	1	0.180	0.0335	0.147	7.5
	2				

TABLE 6-4. Chromium Concentrations in Softener Sludge Leachate by the EP and Texas Toxicity Tests (mg/L)

Test	Total Cr	Cr^{6+}	Cr^{3+}
EP	0.20	0.038	0.125
Texas	0.53	0.29	0.5

CONCLUSIONS

The Texas toxicity test results in a higher chromium concentration in the softener sludge leachate, but extrapolation of the leachate chromium concentration past the seven-day test period suggests that a longer leaching time might more nearly approach equilibrium, yielding a lower leachate chromium concentration close to that obtained with the EP toxicity test. Furthermore, test results do not seem to be affected by the fact that the Texas test attempts to simulate a "mono-disposal" situation, in which the chromium waste is stored separately, while the acidic EP test approximates conditions of "co-disposal." Nevertheless, as it now stands, the Texas toxicity test is a more conservative gauge of a waste's leaching potential than the EP toxicity test--at least with respect to softener sludge.

As far as chromium adsorption is concerned, chromium is favorably adsorbed onto softener sludge at chromium concentrations between 20 and 60 mg Cr/L. further research should involve not only higher concentrations, but also mixtures of chromium and zinc, similar to those commonly found in chrome-zinc corrosion inhibitors.

CHROMATE REMOVAL FROM COOLING WATER BLOWDOWN

Even in the most efficient zero discharge systems, occasions may arise in which it is preferable to perform an "emergency blowdown"--for instance, to dilute high levels of chloride (10,000 ppm) or TOC (600 ppm). In these instances, it is advisable to have a stand-by chromate removal treatment scheme for the blowdown sream to insure that standards are maintained. Experiments with cooling water from the zero-discharge sidestream softening system installed at the USS Chemicals Plant, Pasadena, Texas indicate that chromate removal from high ionic strength water may be accomplished more efficiently and more economically than by the treatment scheme (see Figure 6.8) normally used in continuous discharge systems.

Cr(VI) can be removed from cooling water blowdown by several processes, including (1) chemical reduction to Cr(III) and subsequent precipitation, (2) electrochemical reduction and precipitation, (3) ion exchange, and (4) reverse osmosis. The standard method of hexavalent chromium removal from cooling tower discharge is by chemical reduction and precipitation. This method can be divided into two steps: (1) reduction of Cr(VI) to trivalent chromium (Cr(III)) using reducing agents such as sulfur dioxide, sodium bisulfite, metabisulfite or ferrous sulfate; and (2) precipitation of Cr(III) as $Cr(OH)_3$ by pH adjustment to 8.5 with lime or caustic soda. The precipitated hydroxide is then separated from the blowdown stream. The first step, chemical reduction, requires only a reaction vessel and equipment for adding the necessary reagents (reducing agent, alkali, and acid).

CHROMATE REMOVAL BY REDUCTION WITH FERROUS SULFATE

For years, chromium(VI) has been reduced by addition of ferrous sulfate to remove chromate from blowdown of continuous discharge cooling systems.

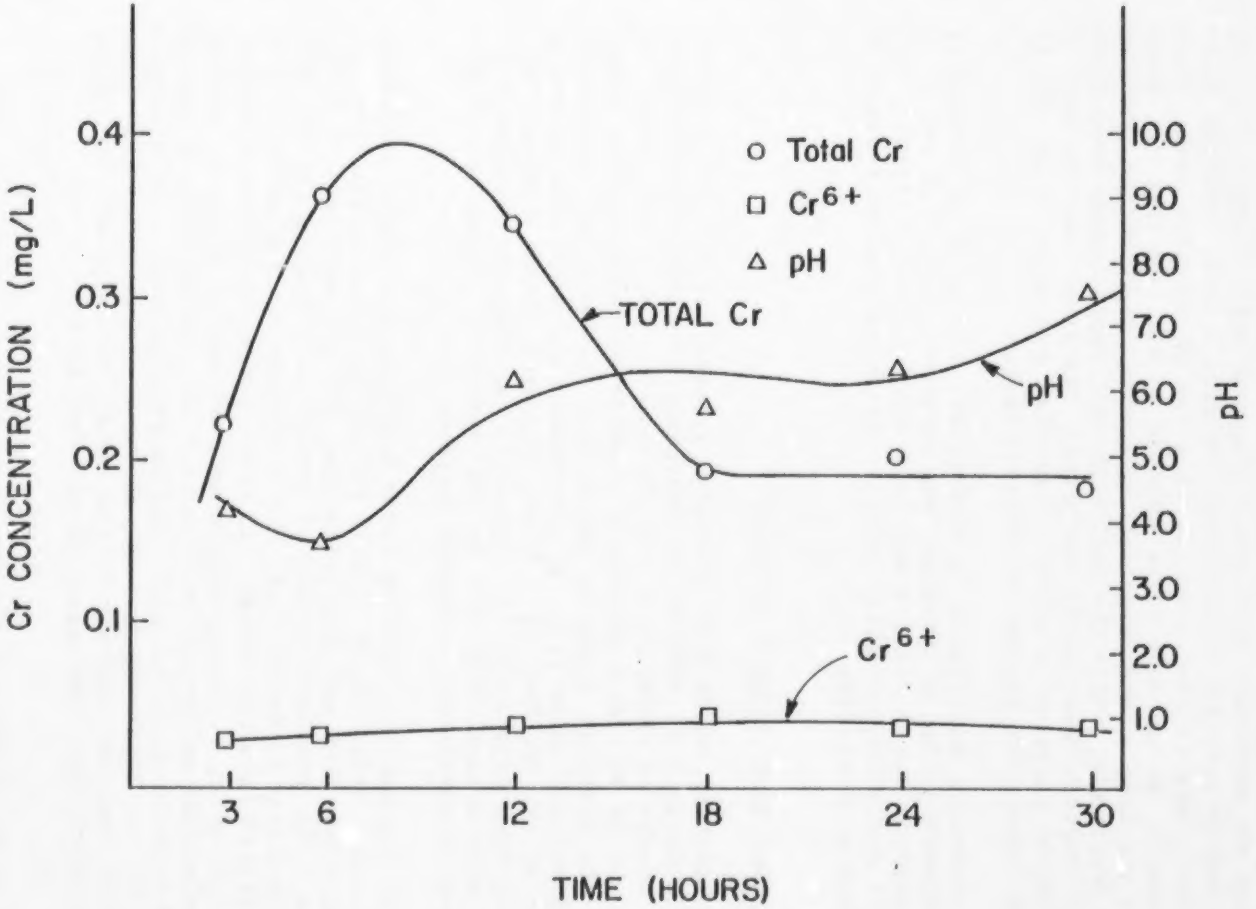


Figure 6-4. Equilibration of EP Toxicity Test for determination of chromate in softener sludge.

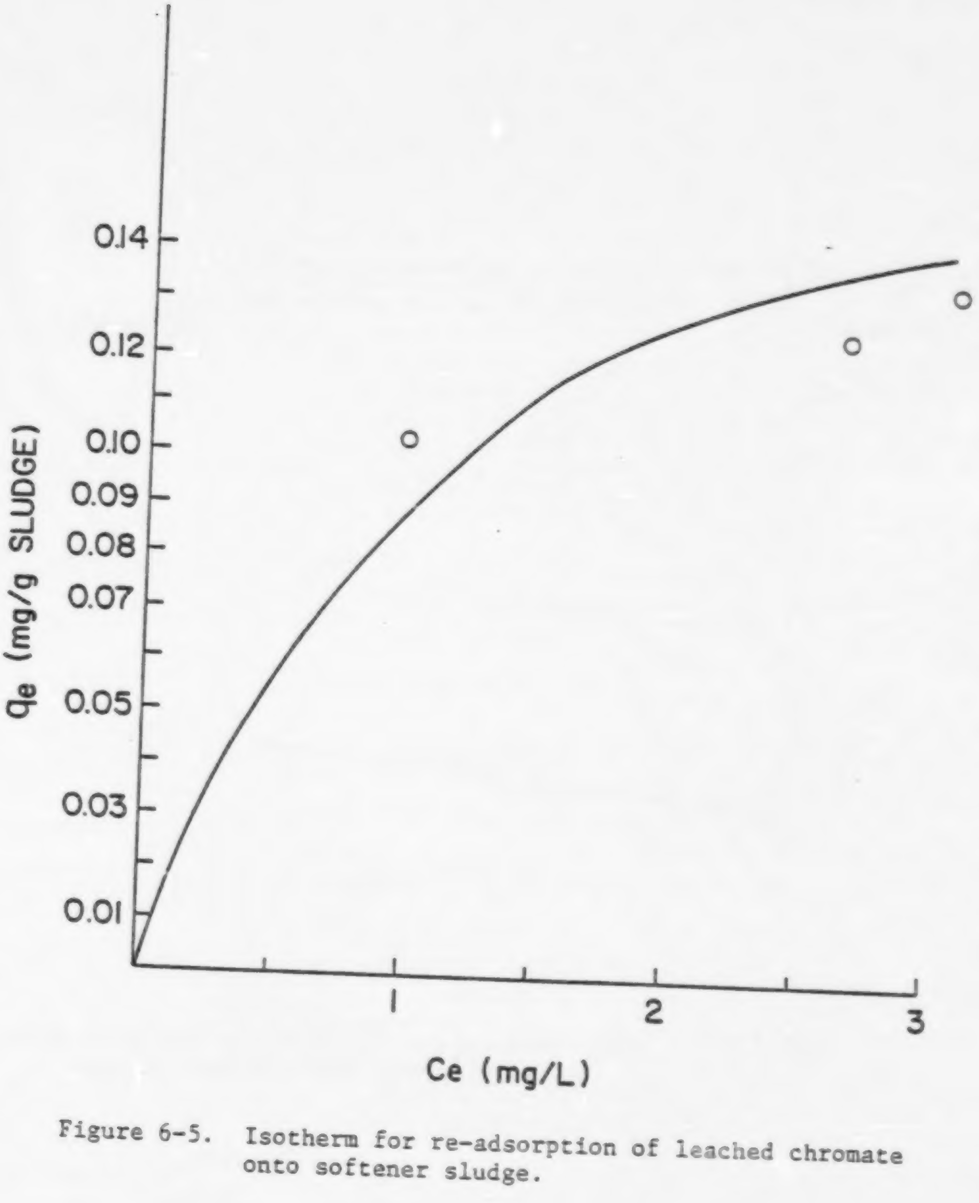


Figure 6-5. Isotherm for re-adsorption of leached chromate onto softener sludge.

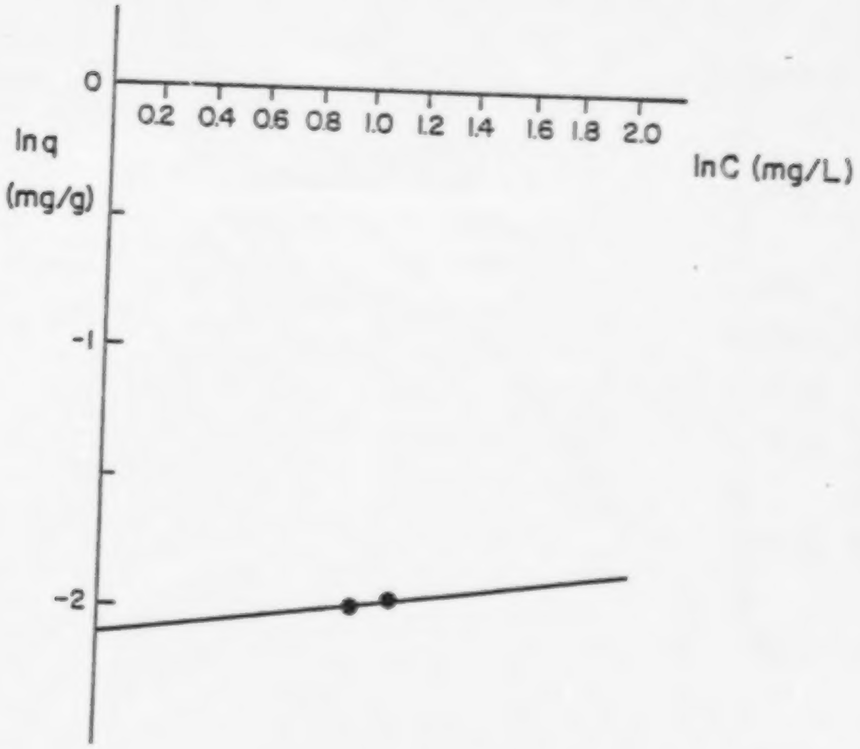


Figure 6-6. Linearized Freundlich isotherm for re-adsorption of leached chromate onto softener sludge.

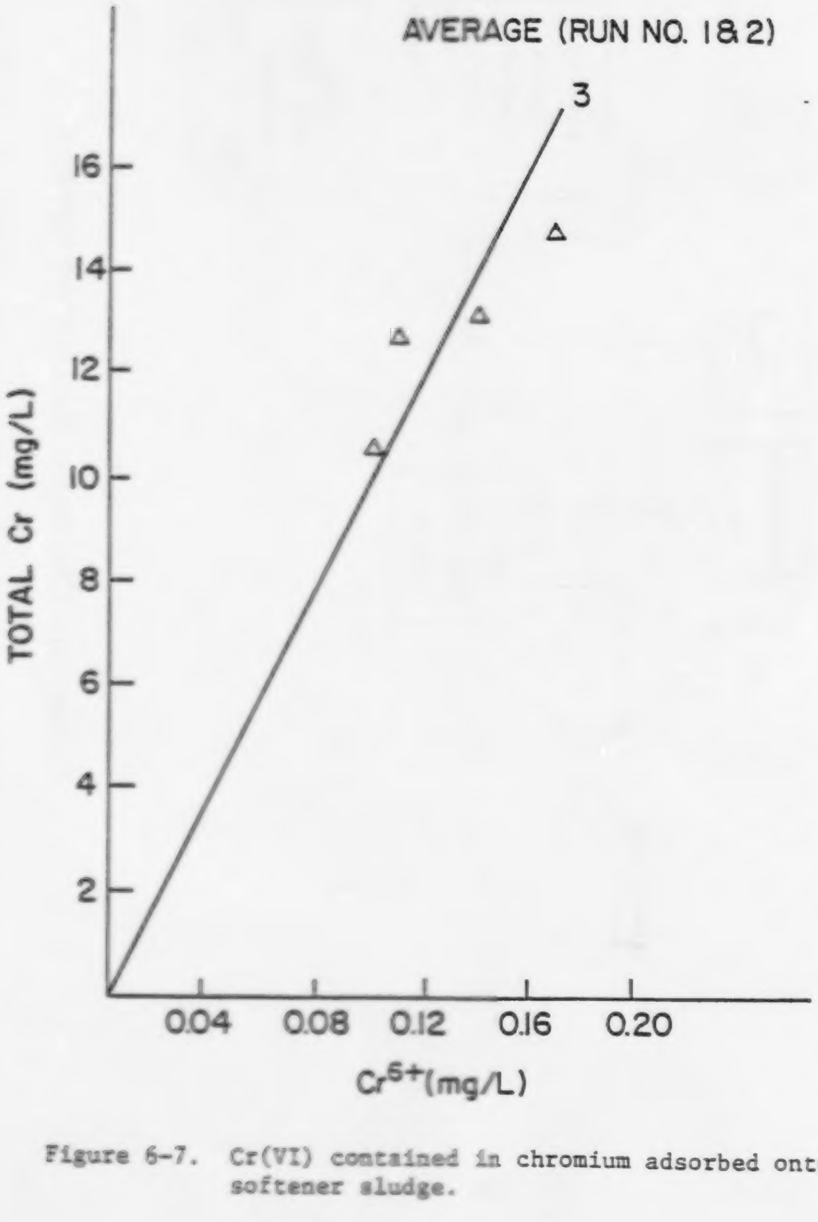
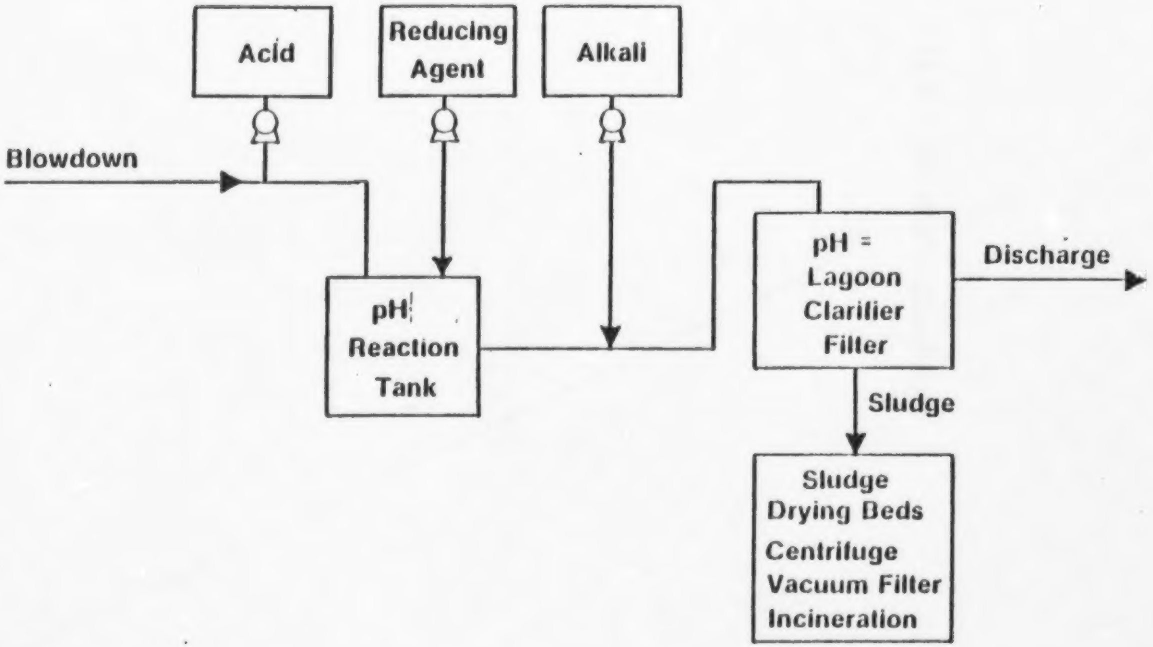


Figure 6-7. Cr(VI) contained in chromium adsorbed onto softener sludge.


Acid
Reducing Agent
Alkali
Blowdown
pH! Reaction Tank
pH = Lagoon Clarifier Filter
Discharge
Sludge
Sludge Drying Beds
Centrifuge
Vacuum Filter
Incineration

Chromate Chemical Reduction System

Figure 6-8. Process schematic for reduction and removal of chromate from cooling tower blowdown.

However, most procedure specifications do not take into account the effects of ionic interaction which occurs in the high TDS cooling waters obtained in zero discharge systems. To make up for this lack of information, chemical removal of chromate by ferrous sulfate reduction in these studies was investigated in two different waters: distilled water, and a high ionic strength cooling water from the USS Chemicals plant. Ferrous sulfate was chosen over other reducing agents (sulfur dioxide, sodium sulfite, bisulfite, or metabisulfite) in order to eliminate the need to lower the cooling water pH with acid prior to reduction.

Removal of hexavalent chromium from cooling water by chemical reduction typically requires four steps:

1. Cooling water blowdown is lowered to between pH 3 - 4 with sulfuric acid to increase the reaction rate of the reduction process;
2. A reducing agent is added to convert Cr(VI) to Cr(III);
3. $Cr(OH)_3$ is precipitated by raising the pH to 8.5 with either lime or caustic soda; and
4. The effluent is clarified to remove the chromium hydroxide floc.

When the reducing agent $FeSO_4$ is used, the following reactions occur:

Reduction

$$\underline{2H_2CrO_4} + 6FeSO_4 \longrightarrow Cr_2(SO_4)_3 + 3Fe_2(SO_4)_3 + 8H_2O$$

Precipitation

$$Cr_2(SO_4)_3 + 6NaOH \longrightarrow 3Na_2SO_4 + \underline{2Cr(OH)_3}$$

The stoichiometric amount of $FeSO_4$ required for Cr(VI) reduction (calculated from the reaction above) is 3.93 mg $FeSO_4$/mg $CrO_4^{=}$. Ferrous sulfate consumption in the reduction reaction is closer to the calculated stoichiometric amount in the pH range of 2 to 5, due to the increased oxidation of the ferrous ion by dissolved oxygen at pH higher than 5. Solubility of the precipitate, $Cr(OH)_3$ is dependent on pH as described in Figure 6-5, with minimum solubility at pH 8.

MATERIALS AND METHODS

The effects on chromate(VI) reduction and removal investigated in this study included ferrous sulfate dosage, pH, and rection and detention times. All experiments were conducted in batch reactors consisting of 250 ml Pyrex beakers containing 100 mL of chromate solution.

The experiments were performed with two different chromate soltuions: an "ideal" low TDS solution prepared from a stock solution of 1000 mg/L potassium chromate (K_2CrO_4) diluted with distilled water to a concentration of 25 mg Cr/L (measured as $CrO_4^=$), and an actual cooling water from the USS Chemicals plant with an average concentration of 25 mg Cr/L. Trivalent chromate solutions were prepared from reagent grade chromium chloride ($CrCl_3 \cdot 6H_2O$).

The pH was adjusted to various values with 0.1 N H_2SO_4. An Orion Digital Ion Analyzer (Model 501) pH meter with hollow body calomel probe was used to measure the various pH parameters of the experiments. Total initial and residual chromium concentrations were determined using a Perkin-Elmer 372 atomic absorption spectrophotometer fitted with a Model HGA-2200 graphite furnace.

Ferrous Sulfate Dose Determination

Procedure to determine the effect of ferrous sulfate dose on chromium (VI) reduction was as follows:

1. Without prior pH adjustment, Cr(VI) was reduced to Cr(III) by addition of varying amounts of ferrous sulfate (100-200 mg $FeSO_4$/L).

2. After a mixing interval of two minutes, 50 mL of the reduced solution was pipetted from the reactor, to which aliquot was added sufficient 0.1 N NaOH to raise the pH to 8.5 and precipitate Cr(III) as $Cr(OH)_3$.

3. The resultant mixture was then filtered through a 0.45 μm membrane filter to remove suspended solids not readily removed by simple sedimentation.

Initial and residual chromium concentrations were measured, with the residual chromium after filtration considered to be unreduced and unprecipitated Cr(VI).

Determination of pH Effects

The three different pH parameters for chromium removal include (1) initial pH of the chromate solution; (2) pH of the solution during reduction (i.e., after addition of $FeSO_4$); and (3) pH of solution for precipitation of $Cr(OH)_4$. For removal of 25 mg Cr/L, a stoichiometric amount of 100 mg $FeSO_4$/L was added to the chromate solution. Procedure for determination of the effect of pH was the same as described above, with the exception that the pH of the solution during the reduction reaction was adjusted to pH 2.5, 4.0, 5.5, and 6.5.

Also, a difference in removal was detected when ferrous sulfate was dissolved at pH 2 or 4 prior to addition to the chromate solution.

Effect of Reaction Time on Chromium Removal

To determine the effect of reduction reaction time on Cr(VI) removal, chromate solution was allowed to contact stoichiometric equivalents of $FeSO_4$ for various times between two minutes and 45 minutes. Following reduction, aliquots of solution were neutralized to pH 8.5, settled, filtered, and analyzed as described above.

Precipitation of Trivalent Chromium

To insure the complete precipitation of Cr(III) from reduced chromate solutions, a solution of trivalent chromium was prepared and precipitated with caustic (NaOH). Precipitation was allowed to proceed for different lengths of time, after which the solution was decanted and filtered and analyzed for chromium. Complete Cr(III) removal was observed at all reaction times greater than two minutes.

Effect of Detention Time on Chromium Removal

After following the Cr(VI) reduction and removal procedure described above with a stoichiometric dose of $FeSO_4$, supernatant solution was allowed to stand for various times from 20 minutes to 48 hours before being analyzed for total chromium. After 24 hours, additional light precipitate was observed; 24 and 48 hour samples were therefore refiltered prior to analysis.

RESULTS AND DISCUSSION

Effect of $FeSO_4$ Dosage on Chromate Removal

The decrease in chromate remaining after increasing dosages of $FeSO_4$ is plotted in Figure 6-8. While, in general, chromate removal improves with increased $FeSO_4$ doses, it is clear that dosages beyond 200 mg $FeSO_4$/L result in increasingly smaller reductions in residual chromate. As a result, the most efficient dosage of $FeSO_4$ appears to be within the range of 100-200 percent of the stoichiometric dose, or (for the given water) 100-200 mg $FeSO_4$/L.

Effect of pH on Chromate Reduction and Removal

Figure 6-9 shows the residual chromate obtained by reduction with $FeSO_4$ at various pH. As can be seen, the greatest chromate removal was achieved when chromate was reduced in deionized water to pH 4.0. This was true regardless of the reaction time allowed for reduction, which had little effect on chromate removal at the optimum pH. However, when reduction took place at pH 2.5, a change in reduction time from two to 45 minutes did seem to have a significant effect on chromate removal.

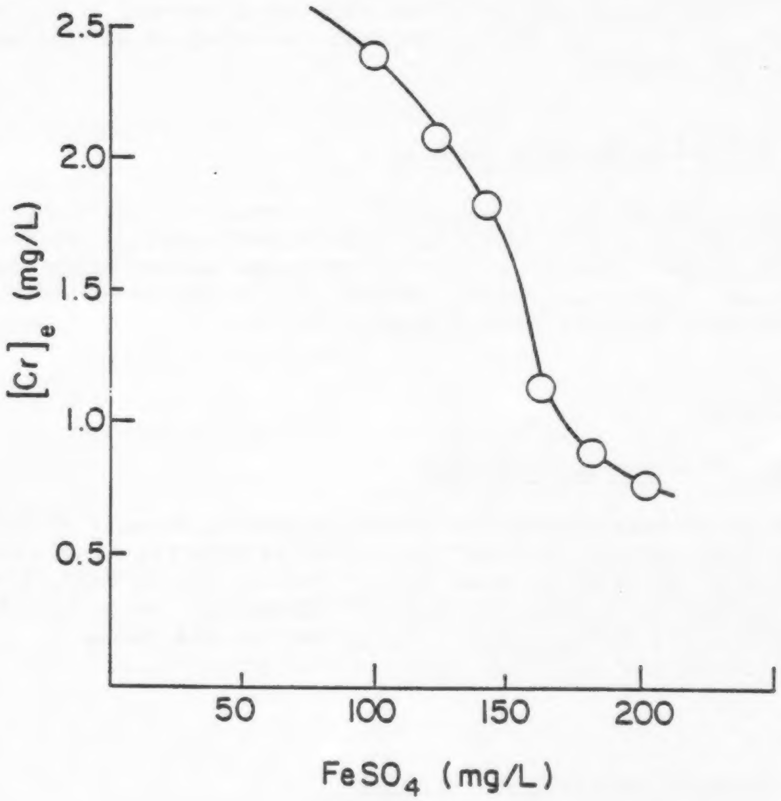


Figure 6-9. Effect of ferrous sulfate dosage on chromate removal from USS Chemicals cooling water.

$Cr_i = 24.3$ mg $CrO_4^=/L$

The effect of reduction pH on removal of chromate from USS Chemicals cooling water is illustrated in Figure 6-10. Unlike the deionized water, cooling water chromate appeared to be more effectively removed when the reduction reaction occurred at pH 6 - 8, with the best removal achieved by addition of an $FeSO_4$ solution acidified to 4.0, which dropped the cooling water pH to 6.9.

The effect of precipitation pH on chromate removal is plotted in Figure 6-11. As can be seen, the lowest chromate residual was obtained when precipitation was carried out at 7.0. This result is contrary to accepted practice, based on the minimal solubility of $Cr(OH)_3$ at 8.5, and suggests that $Cr(OH)_3$ solubility is minimized in the acidic region in cooling waters with high ionic strength.

Effect of Reaction Time on Chromate Removal

The minimal effect of increased reduction time (longer than two minutes) on chromate removal from deionized water has already been inferred from Figure 6-9. Since increased detention time increases the size of the reactor vessel required to accomodate a given flow, it seems clear that a detention time longer than four minutes should not be necessary when the reduction reaction occurs at or near the optimum pH of 4.0. Detention time of the reduction reaction greater than two minutes appeared to have no effect on chromate removal from USS Chemicals' cooling water.

The effect of the time allowed for the precipitation reaction on chromate removal from USS Chemicals cooling water is shown in Figure 6-12. Curiously, the pH of the reduction reaction seems to have had an influence on the speed of the precipitation reaction. When the reduction took place at pH less than 6.0, there was a substantial increase in chromate removal obtained by increasing the precipitation time from 1 to 24 hours. However, when the pH of the reduction reaction was maintained at 6.3, maximum removal during chromate precipitation occurred almost immediately (as shown by the intersection of the residual chromate lines at this pH), and did not seem to improve with time.

CONCLUSIONS

The major finding of this investigation was that chromate can be satisfactorily removed from high ionic strength cooling water without prior acidification by addition of stoichiometric amounts of ferrous sulfate. This modification of usual chromate removal practice would result in substantial savings since no sulfuric acid would be required to lower the pH of the cooling water prior to chromate reduction, and therefore, less caustic would be required to raise the cooling water to pH 8.5 for precipitation and removal of $Cr(OH)_3$.

For USS Chemicals' cooling water, the following scheme appears to result in optimal chromate removal:

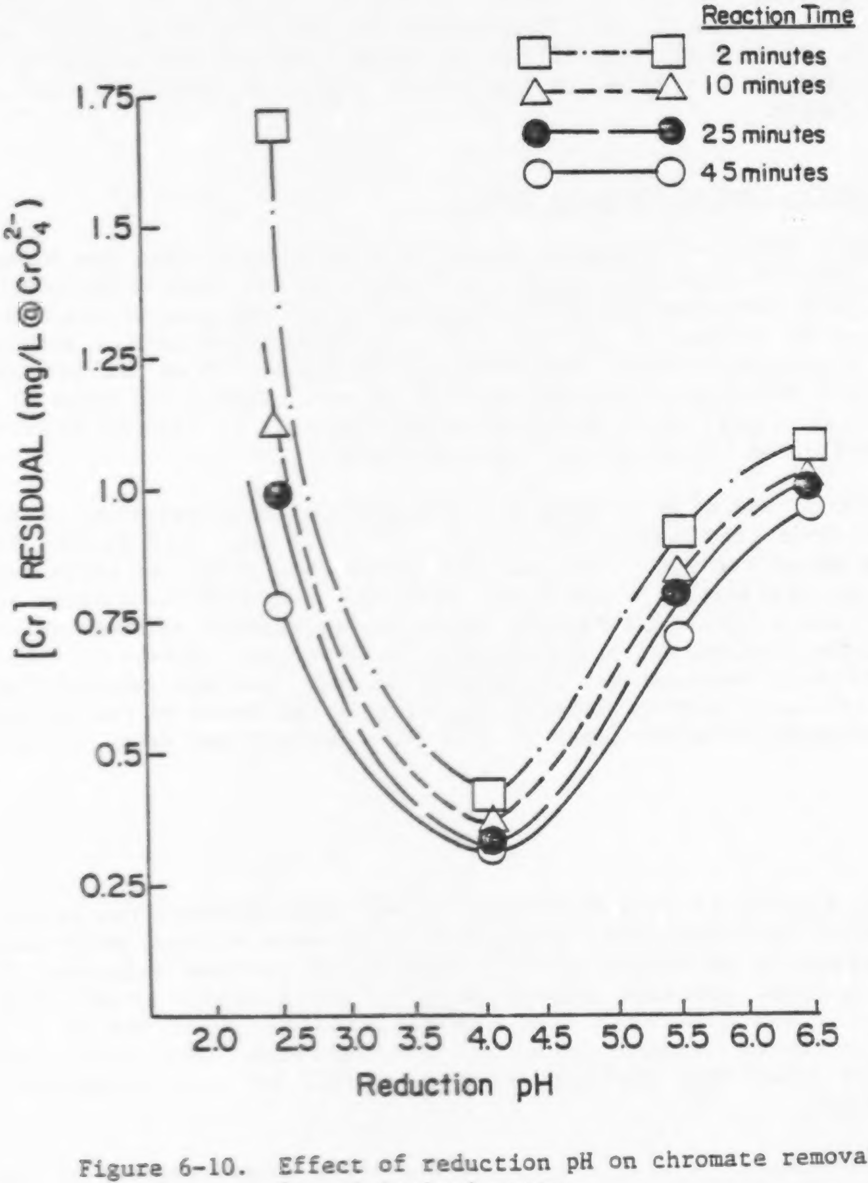


Figure 6-10. Effect of reduction pH on chromate removal. from deionized water.
Cr_i = 25 mg $CrO_4^=$/L $FeSO_4$ = 100 mg/L

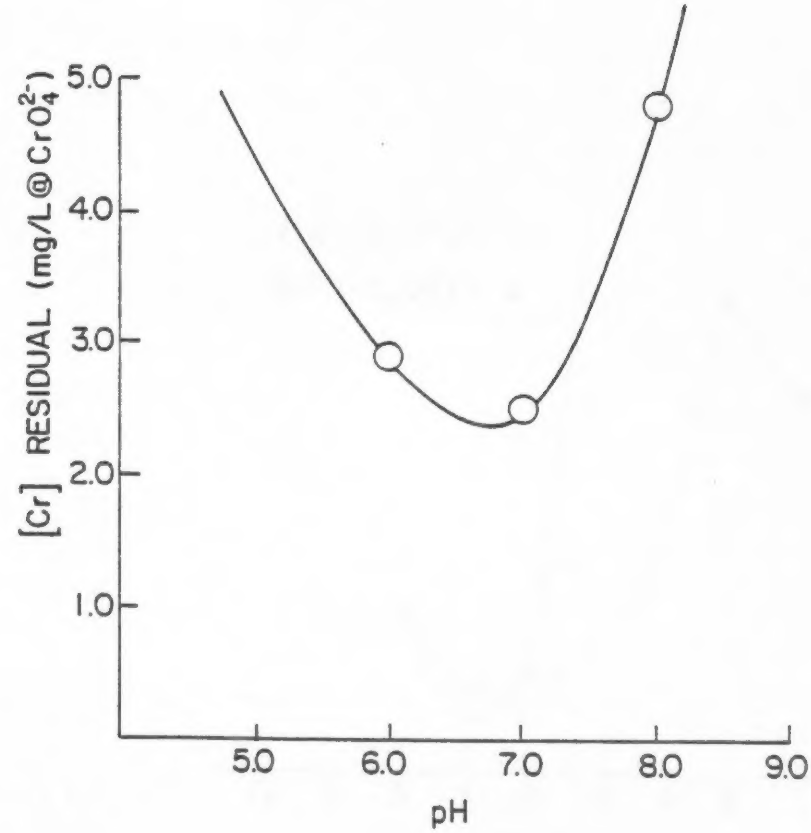


Figure 6-11. Effect of reduction pH on chromate removal from USS Chemicals cooling water.

$Cr_i = 28$ mg $CrO_4^{=}$/L

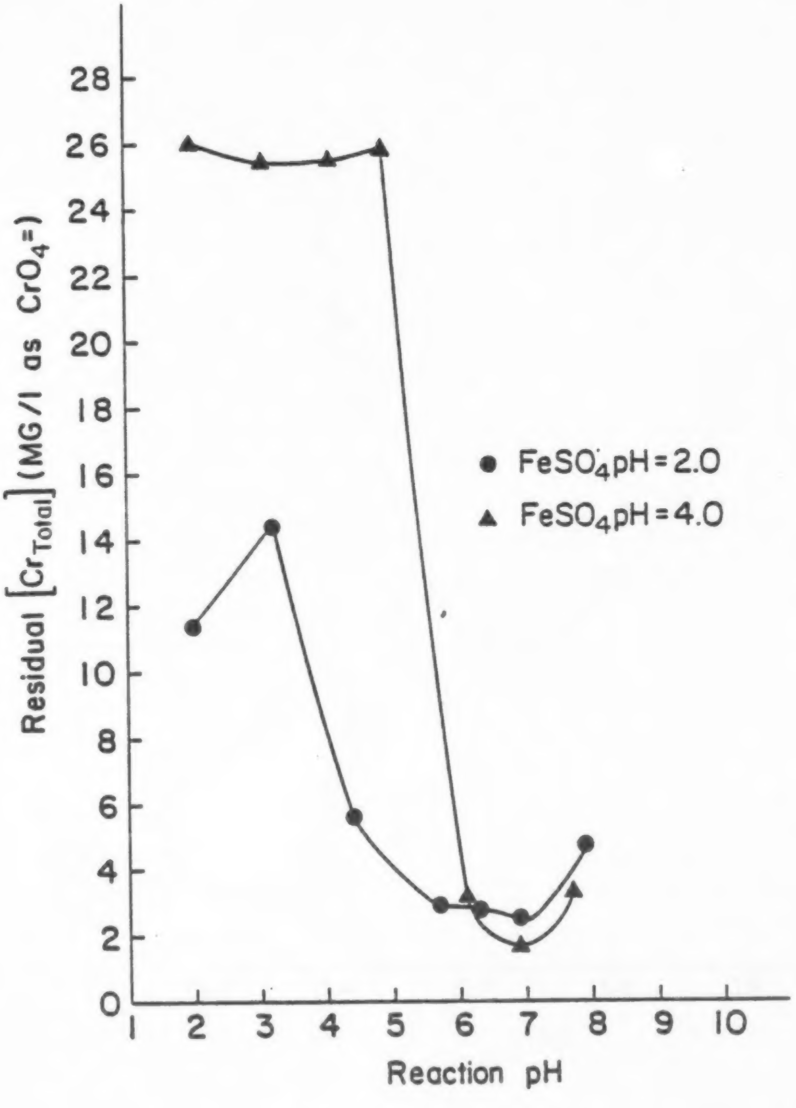


Figure 6-12. Effect of precipitation reaction pH on chromate removal from cooling water.

$Cr_i = 28$ mg $CrO_4^=$/L

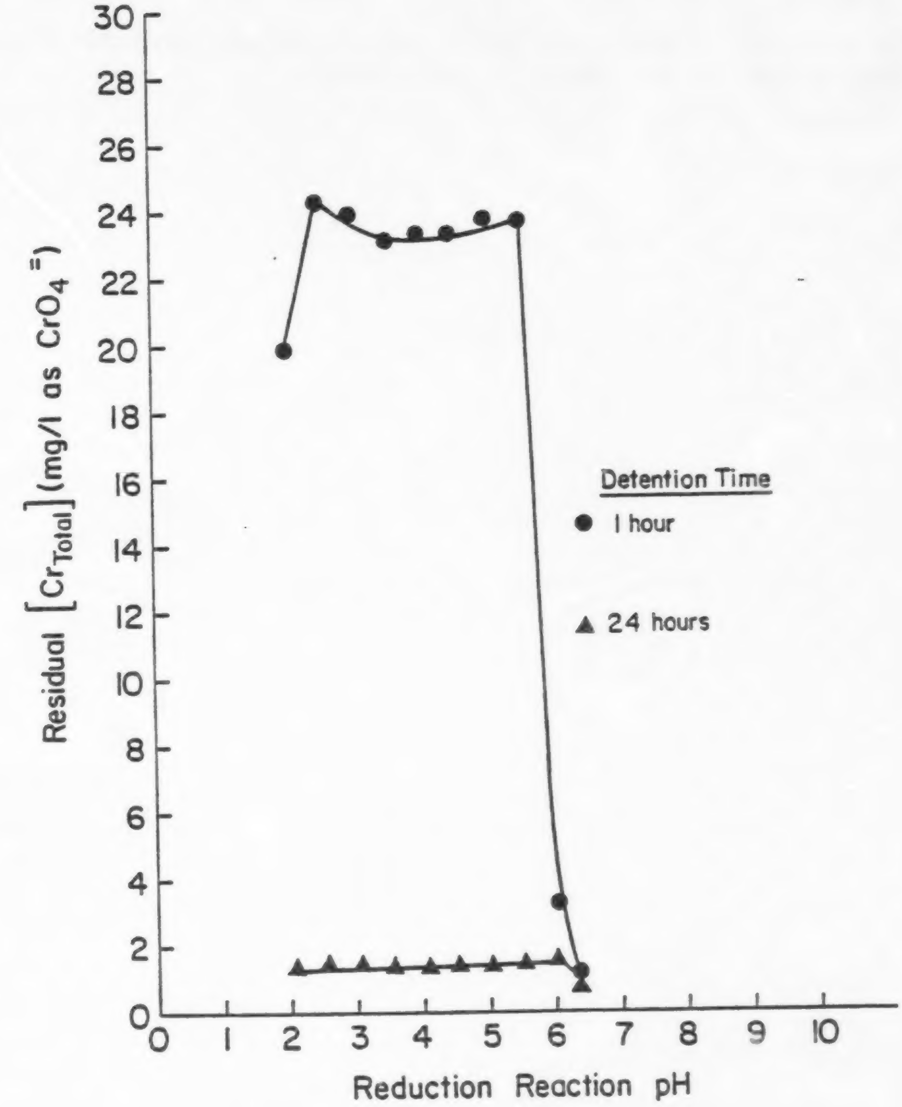


Figure 6-13. Effect of reduction reaction pH on chromate removal from USS Chemicals cooling water at separate settling times.

$Cr_i = 26.8$ mg $CrO_4^{=}$/L

1. A stoichiometric amount of $FeSO_4$ (3.93 mg $FeSO_4$/mg CrO_4^{2-}) is acidified to pH 4.0 and added to the cooling water
2. The cooling water is then mixed continuously for two minutes.
3. The pH of the cooling water is raised to 8.50 with caustic soda to precipitate $Cr(OH)_3$, and mixed for an additional two minutes.
4. The effluent is clarified to remove chromium hydroxide floc (a settling time of 30 minutes is recommended).

SECTION 6 - REFERENCES

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SECTION 7

TOTAL ORGANIC CARBON MASS BALANCE

The objective was to determine the fate of the organic material in the cooling water system. There are basically two sources of organicsfor the cooling water: wastewater treatment unit (WWTU) effluent and treated Trinity River makeup water. Outputs for the above system are: drift, volatiles stripped (from the cooling water) and evaporation (no organics). There is also a biodegradable fraction of organics.

In order to complete the mass balance, experiments were done on the makeup and WWTU water. The purpose was to determine volatile and biodegradable fractions of both influents. Samples from the WWTU (unit) were taken and seeded with microorganisms. Nutrients K_2HPO_4, NH_4Cl, 1.0 g/2 L were added; and the sample was aerated for 12 days. TC and IC were measured and the TOC was determined. The same procedure was uded for samples of the WWTU water but using organisms from the ethylene cooing water and microorganisms from an industrial waste treatment plant, the Washburn Tunnel facility. The TOC results are tabulated in Table 7.1.

A similar method was used for the makeup water. The only difference was the addition of ferrous sulfate in order to avoid incidence of residual Cl_2 on the microorganisms. TOC was measured and the results are tabulated in Table 7-2. Volatile organics fraction jar tests were also done for both samples. For this test, the sample was filtered through a 0.24 μm filter in order to eliminate possible effects of biodegradation by the microorganisms. The samples were bled with air, and initial and final TOC after 24 hours were taken to determine fraction of volatile organics. Results are tabulated in Table 7-1 for WWTU and Table 7-2 for makeup.

To solve the mass balance equation:

$$Q_1C_1 + Q_2C_2 = f_1 Q_2C_2 + f_2 Q_2C_2 + f_3 Q_1C_1 + Q_4C_4$$

C_1: Initial TOC of makeup (18.5)

C_2: Initial TOC of WWTU (63)

Q_1: Flow of makeup water to ethylene cooling tower (635 gpm)

Q_2: Flow of WWTU water to ethylene cooling tower (169 gpm)

f_1: Fraction WWTU volatile (0.1)

f_2: Fraction WWTU biodegradable (0.34)

f_3: Fraction WWTU makeup biodegradable (0.5)

Q_4: Drift loss

C_4: TOC ethylene cooling tower (267.5 ppm)

Solving for drift loss:

$$Q_4 = 45 \text{ GPM}$$

The drift loss flow was calculated by difference to be 45 GPM. This number contrasts with an estimate of 35 GPM by tracer analyses done prior to this research, and 10 GPM by rough TDS mass balances over the system. If the actual drift loss rate is in the 45 GPM range, that means the organics losses are proportioned between biodegradation (31 percent), drift (63 percent), and volatilization (6 percent). With lower estimates of drift loss, biodegradation would have to account for the organics losses.

TABLE 7-1. TOC Results, WWTU

A. Biodegradable Fraction

Time (days)	WWTU (Microorganism Growth) (ppm C)	WWTU (Ethylene) (ppm C)	WWTU (Washburn Tunnel) (ppm C)
0	56	56	56
1	55.2	53	55.2
2	47.0	49.5	49.5
3	-	-	-
4	39.5	42.0	43.5
5	37.5	40.0	41.5
6	37.5	38.5	41.0
7	37.5	37.0	38.5
8	-	37.0	38.5
9	-	-	-
10	-	-	-
11	37.5	-	-
12	-	37.0	38.5

% Biodegradable: 33.93%

B. Volatile Fraction

Time (days)	TOC (Volatile)
0	50
1	45

% Volatile: 10%

TABLE 7-2. TOC Results Makeup

Time (days)	TOC (Ferrous Sulfate Added) ppm C	TOC (No Ferrous Sulfate Added) ppm C
0	11	11
1		
2	9	9.5
3	8.3	9.0
4	7.5	6.8
5		
6	5.5	6.0
7	5.6	6.0
8	5.5	6.0

% Biodegradable: 50%

Volatile Fraction:

Time (days)	TOC (Volatile)
0	11
1	11

% Volatile: 0.0%

SECTION 8

COSTS

The capitol cost of the sidestream softening system is difficult to separate from the total cost of the project. The overall project included a raw water treatment plant to remove suspended solids from Trinity River water. The process equipment included two clarifiers with the chemical feed systems, two multimedia filters, and a pump tank. Common facilities shared with the sidestream softening system were a thickener, rotary vacuum filters, and the control room.

The total project cost based on 1977 dollars was $3.5 million. A 50 percent allocation to the sidestream softening system results in a cost of $1.75 million. This calculates to a cost factor of $2/gallon of flow through the softeners, in terms of capitol cost.

The costs for chemicals in the softening system and for the cooling water system were closely followed. In Table 8-1, the chemical costs for the lime softening system on an average cost per day basis are shown. In Table 8-2, the costs are on the basis of cost per thousand gallons. For the latter case, the costs averaged $.37/1000 gallons for the time period studied. The number compares favorably with costs greater than $1/1000 gallons for processes such as ion exchange, and reverse osmosis.

For the cooling water system, the chemical usage is indicated in Table 8-3. The chemicals include the dispersants, inhibitors, biocides, and carbon dioxide. The chemical cost per unit gallons recirculation water is shown in Table 8-4. The total cost for the period studied was $0.16/1000 gallons, which is comparable to the costs in a normal recirculating water system if sulfuric acid costs were substituted for carbon dioxide costs as it would be in a typical cooling water system.

Figure 8-1
Chemical Cost for Lime Softening System

Dates	No. Days	Lime $79.15/Ton Cost	 Cost/Day	Soda Ash $0.1075/# Cost	 Cost/Day	CO_2 $53.00/Ton Cost	 Cost/Day	Sludge* $9.88/Ton Cost	 Cost/Day	Σ Cost	Σ Cost/Day
3/5-3/25	21	3,480.30	165.73	827.75	39.42	556.50	26.50	722.52	34.41	5,587.07	266.05
3/26-4/15	21	3,218.79	153.28	1,677.00	79.86	556.50	26.50	515.68	24.56	5,967.47	284.17
4/16-5/6	21	3,938.90	187.57	2,123.12	101.10	556.50	26.50	882.09	42.00	7,500.61	357.17
5/7-5/27	21	3,377.88	160.85	1,752.25	83.44	556.50	26.50	601.94	28.66	6,288.57	299.46
	Σ	14,015.87		6,380.12		2,226.00		2,722.23		25,344.22	1,206.87
	Ave Cost/Day		166.86		75.95		26.50		32.41		301.72

* Based on average weight of 12.88 tons lime sludge/load and $127.00/load, cost is approximated as $9.88/tons. This checks within 5% of cost by summation of loads disposed.

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Figure 8-2
Chemical Cost Per Unit Gallons Water Treated

Date	No. Days	1000 Gal / Day	Lime Cost / 1000 Gal	Soda Ash Cost / 1000 Gal	CO_2 Cost / 1000 Gal	Sludge Cost / 1000 Gal	Σ Cost / 1000 Gal
3/5-3/25	21	815.34	0.2033	0.0483	0.0325	0.0422	0.3263
3/26-4/15	21	837.90	0.1815	0.0945	0.0314	0.0291	0.3365
4/16-5/6	21	792.70	0.2309	0.1245	0.0326	0.0517	0.4396
5/7-5/27	21	758.61	0.2129	0.1104	0.0351	0.0380	0.3964
	Ave Cost / 1000 Gal	801.14	0.2072	0.0944	0.0329	0.0403	0.3747

Figure 8-3

Chemical Usage For Cooling Water System

Dates	No. Days	Ca Dispersants lbs	Zinc Inhibitor lbs	Chromate Inhibitor lbs	Non-Oxidizing Biocide lbs	Chloride lbs	Bromine lbs	CO_2 lbs
3/5-3/25	21	70.26	773.62	368.04	415.45	320.88	1,064.0	225,260
3/26-4/15	21	57.17	1,365.29	520.33	1,163.26	6,651.96	1,280.0	304,720
4/16-5/6	21	158.05	1,282.38	717.04	664.72	7,438.41	1,967.0	349,250
5/7-5/27	21	83.43* 77.09	1,105.50	621.86	NIL	7,152.60	981.0	298,300
	Ave lbs / day	-	53.89	26.51	26.71	256.71	63.00	14,018.21

* Split poundage due to addition of new calcium dispersant to cooling water.

Figure 8-4
Chemical Cost Per Unit Gallons Recirculation Water

Period	Dates	Ca Dispersant $\frac{\text{Cost}}{\text{1000 Gal}}$	Zinc Inhibitor $\frac{\text{Cost}}{\text{1000 Gal}}$	Chromate Inhibitor $\frac{\text{Cost}}{\text{1000 Gal}}$	Non-Oxidizing Biocide $\frac{\text{Cost}}{\text{1000 Gal}}$	Chlorine $\frac{\text{Cost}}{\text{1000 Gal}}$	Bromine $\frac{\text{Cost}}{\text{1000 Gal}}$	CO_2 $\frac{\text{Cost}}{\text{1000 Gal}}$	$\frac{\Sigma\ \text{Cost}}{\text{1000 Gal}}$
I	3/5-3/26	0.0013	0.0055	0.0042	0.0090	0.0005	0.0341	0.0638	0.1184
II	3/26-4/15	0.0011	0.0098	0.0060	0.0251	0.0103	0.0410	0.0863	0.1795
III	4/16-5/6	0.0029	0.0092	0.0083	0.0143	0.0115	0.0630	0.0989	0.2082
IV	5/7-5/27	0.0025	0.0079	0.0072	0.0	0.0111	0.0314	0.0845	0.1446
	Σ	0.0078	0.0324	0.0257	0.0484	0.0334	0.1395	0.3335	0.6507
	$\frac{\text{Ave Cost}}{\text{1000 Gal}}$	0.0020	0.0081	0.0064	0.0121	0.0084	0.0349	0.0834	0.1627

[*] Figures based upon a 21-day period and 93,600 1000 gal recirculating/day.

SECTION 9

ZERO DISCHARGE SIDESTREAM SOFTENING AT TOSCO

INTRODUCTION

In response to needs for water conservation and environmental protection, the TOSCO Corporation elected to install a side stream softening system at their Bakersfield, California petroleum refinery. This plant site is typical of small to medium sized refineries except that it is located in a semi-arid region. Local and federal governments had imposed significant incentives to reduce freshwater consumption and to protect groundwater resources. This environment led TOSCO to initiate engineering studies for water conservation in 1975. Since blowdown from the open cooling water system comprised a major portion of the plant wastewater, these studies included a review of existing technology for the recovery and recycle of the blowdown. In early 1980, a conceptual process design was prepared for a sidestream softening process to enable the recycling of cooling tower, a particulate scrubber and boiler blowdown streams. This design was unique in that it combined treatment and recycle of waste streams other than cooling tower blowdown into a single treatment system. TOSCO accepted the conceptual process and proceeded with final design and construction. The wastewater recycling facilities, based upon a caustic softening process, were started up in early 1982.

The objective of this report is to compare the predicted performance of the conceptual process design to the actual performance of the completed plant. The TOSCO sidestream softening system is well suited for this purpose since only very minor changes were made in the process design during final engineering and construction. The general features of the conceptual design are reviewed. The design methodology is summarized, with emphasis on the techniques used for chemistry calculations and prediction of process performance. The various process alternatives that were investigated are contrasted in this report, with discussion of potential advantages and disadvantages. The final process design is also briefly reviewed. Process changes made during final engineering can have a significant impact upon actual performance of the softening system. A comparison between predicted and actual performance is also presented. Relevant factors contributing to these comparisons are identified and discussed. This comparison provides a convenient basis for the formulation of recommendations concerning the design procedure used for caustic softening and recyclingof blowdown streams to an open, recirculating cooling water system. These are presented in the final section.

GENERAL PLANT DESCRIPTION

TOSCO Corporation is a medium sized independent oil refining and petrochemical company. A small refinery near Bakersfield, California was owned and operated by TOSCO until adverse economic conditions forced a shutdown in 1983. The plant incorporated the conventional processes found in most crude oil refining plants, including distillation, catalytic cracking, and coking processes plus steam and cooling water utility systems. The Bakersfield plant is located in an agricultural area with annual rainfalls averaging less than 12 inches annually. Petroleum refining is also of major economic importance. Thus, the Bakersfield area is in a semi-arid climate with a significant economic dependence upon both irrigation and groundwater. With the scarcity of surface water and the importance of the agricultural industry, very stringent requirements are placed on discharges to receiving streams. Similarly, dependence upon groundwater for potable supplies and irrigation requires strict regulation of waste holding ponds and disposal wells. The superfund taxes, based upon volume of waste injected into disposal wells, represented a significant wastewater disposal cost. Prior to the startup of the sidestream softening system, most process wastewater and blowdown streams were disposed of by deep well injection.

The major wastewater streams at the TOSCO refinery included cooling tower blowdown, boiler blowdown, thermal catalytic cracking (TCC) unit scrubber blowdown, coker scrubber blowdown, and sour water stripper bottoms. Of these streams, coker scrubber blowdown could not be considered for recycle due to the presence of very fine solids, dissolved organics, and reduced chemicals. This stream was disposed of by clarification, filtration, and deep well injection. Flow and water quality data for the remaining streams are presented in Table 9.1. Although the sour water stripper bottoms represented a large waste load and was of high quality in many respects, it was decided to exclude this stream from the wastewater recycling project. At times the ammonia and sulfide concentrations would become very high. The presence of these materials within a cooling tower system could present unique corrosion problems. Earlier studies conducted at the TOSCO plant indicated that the quality of the remaining waste streams was acceptable for recycling following suitable physicochemical treatment.

The cooling water system used at the TOSCO plant in Bakersfield presented a unique situation also. The plant operated with a total of five cooling towers. Four of these towers (Nos. 1-4) operated from a common basin. Blowdown from cooling tower No. 5 discharged directly into this common basin. The blowdown stream from the No. 5 tower therefore served as a feed or makeup stream for towers No. 1-4. With this flow scheme it was possible to treat the four cooling towers as a single unit. The combined recirculation rate of the five towers is about 53,000 gpm. A relatively hard wellwater was used to provide makeup water for the cooling tower system, as noted in Table 9.1. The heat exchange system served by the cooling towers was mostly constructed of mild steel. This situation made the continued use of chromate based corrosion inhibitors a major benefit for selection of the sidestream softening system. A chemical softening process treating a sidestream from the cooling towers would permit recycle of chromates, eliminating the environmental impact of a toxic chemical.

Before the wastewater recycle plant was completed, wastewater at the TOSCO plant was discharged either to an evaporation pond or disposal well. Local and state agencies had imposed very strict standards for operation of waste ponds and disposal wells. These governments were also exerting pressure for industry to reduce its reliance upon both surface and groundwater resources. The superfund tax burden for deep well injection of cooling tower and boiler blowdown was in excess of $350,000 annually. In addition, the cost for operation and maintenance of the injection well was strongly influenced by the volume of wastes handled. These incentives were in concert with improved corrosion protection that would be obtained by recycling of chromates. For these reasons TOSCO decided to proceed with design and construction of a sidestream softening system for the recovery and reuse of several wastewater streams.

SIDESTREAM SOFTENER PROCESS DESIGN, TOSCO REFINERY

The process design for the zero blowdown sidestream softening system for the TOSCO refinery will be reviewed in this section. The methods and assumptions used in the preliminary process design will be discussed and related to predicted performance. The TOSCO design provides a very interesting example for application of techniques used for softener design. The process used was unique in combining scrubber blowdown with sidestream softening. The cooling water system used at the Bakersfield refinery presents an interesting flow pattern. Design equations were developed for this process. The final design will also be briefly reviewed in this section. Changes in preliminary design inevitably occur as final design and construction are completed. These differences will serve as a comparison of preliminary and final designs.

PRELIMINARY PROCESS DESIGN

It was noted above that the cooling water system used at the TOSCO refinery was unusual. The centralized basin and cooling towers 1-4 can be treated schematically as a single cooling tower system. This system, however, receives two feed streams rather than the conventional single feed. Fresh wellwater is added to replace evaporation, drift, and blowdown. The blowdown stream from cooling tower 5 is also added to the central basin. This is a low quality water that represents a significant load of scale forming salts for the combined cooling water system. It was also decided to include boiler blowdown and TCC scrubber blowdown in the sidestream softener design. No changes in operation were anticipated for cooling tower 5. This multiple cooling tower system is much more complex than systems typically described in the literature. Unique mass balance relationships were derived for the TOSCO system. Using these design models, equilibrium chemical calculations, and assumptions based upon previous experience, a detailed prediction of final cooling water quality was performed for the process recommended to TOSCO. These calculations will be reviewed in this section.

The sidestream softening process recommended for the above cooling water system is represented schematically in Figure 9.1. Definitions for the symbols used in this schematic are included in this figure. This schematic shows the No. 5 cooling tower blowdown (Q_{CT}) being added to the central basin while boiler blowdown (Q_b) and TCC scrubber blowdown (Q_{TCC}) are directed to the sidestream softening system. The boiler blowdown provides a significant source of both silica and alkalinity for the softener, as shown in Table 9.1. The alkalinity would reduce requirements for soda ash within the softener and silica will be removed during the softening process. The TCC scrubber blowdown can contain high suspended solids levels but otherwise provides a good quality makeup source. These solids can be removed within the softening system. In this process the softener removes scale components (i.e., Ca, Mg, and SiO_2) from cooling water and permits recycle of two wastewater streams.

The sidestream softening system described by Figure 9.1. is unique to the TOSCO plant. A steady state mass balance model is required to size the softener and clarifier. Based on these mass balance equations, cooling water quality and chemical dosages can be estimated. The scale constituent(s) that determine sidestream flow to the softener can also be identified, as discussed in a previous chapter. Steady state mass balances must be developed for water, non-conserved soluble species, and conserved species passing through the sidestream softener. Effects of all chemical additives must be considered when designing a sidestream softener since all salts will become highly concentrated in a zero blowdown system. Additives such as H_2SO_4 can affect scale formation, e.g., sulfuric acid may cause $CaSO_4$ scale to form within heat exchangers. The development of these mass balance equations and their use of estimating softener size and cooling water quality will be considered in subsequent sections of this chapter.

MASS BALANCE EQUATIONS

The schematic diagram of the cooling water system suggests that mass balances may be performed for the cooling tower/sidestream softener as a single system. Mass balances may also be performed for subsystems consisting of the cooling tower and softener separately. The proper system or subsystem for analysis must be selected in order to obtain desired information concerning process design. The first step is usually to quantify flowrates of all input and output streams by performing a water balance. Since the flow rate to and from the softener is unknown, the entire system should be selected for the water balance. Based upon Figure 9.1 this water balance is given below:

$$Q_M + Q_A + Q_{CT} + Q_b + Q_{TCC} Q_C - Q_e + Q_d + Q_w \tag{9-1}$$

All flow terms in Equation 9.1 with the exception of makeup, Q_M, softener chemical additions, Q_C, and waste softener sludge, Q_W, are known from plant operating experience. These known flowrates are included in Table 9.1. Reasonable estimates for Q_A, Q_C, and Q_W, based on prior experience, can be used to quantify these terms. Using these assumptions, Equation 9-1 can be used to estimate the makeup flowrate, Q_M.

The next objective is to estimate the required flowrate discharged to

TABLE 9-1. WATER QUALITY DATA BASE

Water Source	$Q_{(gpm)}$	Ca*	Mg*	M.Alk.*	SiO_2	Cl	SO_4	Na	pH	TSS**	NH_3	H_2S
No. 8 Well	-	100	33	106	17	36	72	45	8.4	-	-	-
No. 5 CT blowdown	55	440	120	24	140	330	783	342	7.0	-	-	-
Boiler blowdown	50	-	-	550	125	363	480	718	11.1	-	-	-
Sour water stripper bottoms***	130	6	1	-	3	-	-	-	-	-	5	5
TCC Scrubber blowdown	25	50	24	100	21	24	60	56	8.4	6,700	-	-

*Concentrations in ppm $CaCO_3$. All other concentrations are mg/L.

**Total suspended solids.

***Ca, Mg, and SiO_2 per D. Miller, 3/26/80, except NH_3 and H_2S.
Na concentrations calculated for electroneutrality

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the sidestream softener, Q_s. This flowrate, in conjunction with estimated water quality, determines the size of the softener. The magnitude of Q_s is estimated by performing a soluble species balance around the cooling tower subsystem. This mass balance equation appears as follows:

$$Q_m C_m + Q_A C_A + Q_{CT} C_{CT} + Q_T C_T = Q_d C_w + Q_s C_w \tag{9-2}$$

It should be noted that Equation 9-2 is not valid for species which can be strongly influenced by aqueous equilibria such as CO_2, HCO_3^- and $CO_3^=$. All flow terms in Equation 9-2 are known except for Q_s and Q_T. These flowrates can be related by a water balance around the softener subsystem:

$$Q_T = Q_s + Q_b + Q_{TCC} + Q_c - Q_w \tag{9-3}$$

Combining Equation 9-2 and 9-3 and solving for Q_s yields the following design equation:

$$Q_s = \frac{1}{C_w - C_T} [(Q_M + Q_A) C_M + Q_{CT} C_{CT} + (Q_b + Q_{TCC} + Q_c - Q_w) C_T - Q_d C_w] \tag{9-4}$$

For Equation 9-4 it was assumed that $C_A = C_M$ for important scale forming species. Equation 9.4 can be used to estimate the flowrate to the softener, Q_s, by using known flowrate and concentration data in addition to estimated concentrations for the softener effluent. Application of Equation 9-4 to each scale forming species that may limit cooling water concentration, i.e., $CaCO_3$, $CaSO_4$, and SiO_2, must be performed to determine the required flowrate to the softner. Maximum concentrations within the cooling water, C_w, can be determined from prior experience with actual cooling water systems. Concentrations for softener effluent can be obtained either from jar testing on simulated cooling water or from prior experience with sidestream softening. For the TOSCO design, the estimated softener effluent quality was based upon jar testing conducted by the NUS Corporation.

The concentration for both conserved and non-conserved soluble species within the cooling water must also be estimated during process design. The equation used for non-conserved species (i.e., Ca^{+2}, Mg^{+2}, SiO_2, Alkalinity) can be obtained directly from a mass balance around the cooling tower subsystem, Equation 9-2:

$$C_w = \frac{1}{Q_s + Q_d} [(Q_M + Q_A) \quad C_M + Q_{CT} + C_{CT} + Q_T C_T] \tag{9-5}$$

The desired C_w for the limiting scale species is used to estimate Q_s and Q_T. Values of C_w for remaining non-conserved species are estimated using Equation 9-5. Conserved species in the cooling water (e.g., Cl^-, $50 = Na^4$, etc.) can be influenced by chemical additions such as Na_2CO_3, H_2SO_4, or chromate salts. It is therefore desirable to include each input stream individually in the equation used for conserved species. This equation can be obtained by performing a mass balance around the entire system shown in Figure 9-1. Performing this balance and solving for cooling water concentration, C_w, yields the following:

$$C_w = \frac{Q_2}{Q_1 Q_2 - Q_T Q_S} \left[Q_M C_M + Q_A C_A + Q_{CT} C_{CT} + \frac{Q_T}{Q_2} (Q_b C_b + Q_{TCC} C_{TCC} + Q_C C_C) \right] \tag{9-6}$$

where

$$Q_1 = Q_d + Q_s \tag{9-7}$$

$$Q_2 = Q_T + Q_w \tag{9-8}$$

Equation 9-6 was used to estimate cooling water quality for all conserved species. Prior to application of Equation 9-6 for conserved species it is necessary to estimate required dosages of softening, neutralization, and cooling water chemicals. These calculations will be discussed in the next subsection.

CHEMICAL DOSAGE CALCULATIONS

A sidestream softener for a zero blowdown cooling water system must remove both calcium and silica to prevent scale formation. Calcium is precipitated as $CaCO_3$ while silica (SiO_2) is removed with $Mg(OH)_2$ that forms as magnesium precipitates. The important softening reactions are shown in Table 9-2. A base, usually lime, is added to raise pH and initiate precipitation. Soda ash (Na_2CO_3) is added to balance calcium hardness and improve calcium removal. Magnesium is often added, either as dolomitic lime or as a soluble salt (e.g., $MgSO_4$) to improve silica removal in the softener. After softening reactions have been completed, the water must be neutralized prior to returning to the cooling tower basin by addition of an acid. Sulfuric acid is usually used for neutralization, but care must be exercised to avoid conditions leading to calcium sulfate scale formation. The estimation of these dosages will be described in this subsection.

The pH of the cooling tower can be raised using either lime (CaO) or caustic soda (NaOH). The selection of either chemical must be based upon the overall economics of the process. While lime is generally cheaper than NaOH, it increases the soda ash requirement, produces more sludge, and requires more complex handling equipment. The high cost of soda ash, sludge disposal, and maintenance cost may lead to choice of NaOH rather than lime. This choice is site specific, however. The required dosage of base is estimated using the method of Matson (1,3). Matson recommends the following equation:

$$\underset{(\text{ppm } CaCO_3)}{\text{Base Dosage}} = CO_2 + HCO_3 + MgH + SiO_2 + \Delta OH \tag{9-9}$$

In Equation 9-9, the quantities on the right side represent cooling water values expressed in ppm $CaCO_3$. The value of OH is obtained from the change in pH from cooling water to softener values. Assumptions must be made at this point concerning cooling water pH, alkalinity, and softener pH. Equation 9-9 may be used to estimate the dosage of NaOH or CaO.

The addition of soda ash (Na_2CO_3) is used to improve removal of calcium hardness. The usual practice, as recommended by Matson (1,3) is to obtain a balance between calcium hardness and available carbonate. Using this as the objective, the following equation is used:

$$\begin{matrix} Na_2CO_3 \text{ Dose} \\ (\text{ppm } CaCO_3) \end{matrix} = \text{CaH} + \text{Lime Dose} - CO_2 - 2(HCO_3) - CO_3^- \qquad (9\text{-}10)$$

Again, all values to the right of the equal sign are in ppm $CaCO_3$. Equation 9.10 shows the relationship between soda ash dose and lime dose. If NaOH is used to raise cooling water pH, the second term on the right side of Equation 9-10 is zero.

Estimation of magnesium requirements must consider the degree of removal for silica. Matson (1) has shown that SiO_2 removal in sidestream softeners follows a Freundlich isotherm:

$$q_e = kC^n \qquad (9\text{-}11)$$

where qe is the mass ration of silica removal to magnesium removal, C is the SiO_2 concentration in the softener effluent, and both k and n are empirical constants. Values of k and n are dependent upon temperature, and were discussed previously in this report. For any softener flowrate, Q_s, there will be some maximum value for SiO_2 in the softener effluent that must be maintained to prevent SiO_2 scaling. Using this value on available Mg and isotherm data are compared. If the available q_e is greater than the isotherm q_e, Mg must be added. The dosage of Mg can easily be calculated from the two values of q_e. A soluble magnesium salt, $MgSO_4$, was considered for the TOSCO design since improved SiO_2 removal has been found for this form of magnesium (1). It should be noted that addition of a magnesium salt would increase the required dosage of base, as shown by Equation 9-9.

As a final check of accuracy for the above water quality and dosage calculations, check is performed for electroneutrality. Total positive and negative equivalent concentrations are calculated for the estimated cooling water quality. If these values are sufficiently close, the calculations are accepted. If not, the entire process is repeated, using the results of the previous iteration where necessary.

PRELIMINARY DESIGN RESULTS

The calculation methods described above were applied to the TOSCO

TABLE 9-2. SOFTENING REACTIONS

Carbonic Acid System:

$$H_2CO_3 + OH^- \quad H_2O + HCO_3^-$$

$$HCO_3^- + OH^- \quad H_2O + CO_3^=$$

Precipitation:

$$Ca^{2+} + CO_3^= \quad CaCO_{3(s)}$$

$$Mg^{2+} + 2OH^- \quad Mg(OH)_{2(s)}$$

Adsorption/Coprecipitation:

$$SiO_2 + Mg(OH)_{2(s)} \quad SiO_2 \cdot Mg(OH)_{(s)}$$

TABLE 9-3. PROJECTED WATER BALANCE

Item	AVG	MAX
Makeup Water*	1518 gpm	1518 gpm
No. 5 CT Blowdown	55	55
Boiler Blowdown	50	50
TCC Scrubber Blowdown	25	25
Evaporation (30° F T)	1590	1590
Drift	53	53
Treated Water Return	235	400
Blowdown, CT Nos. 1 - 4	165	330
Softener Flow**	245	410
Sludge Flow	10	10

* Includes 1 gpm flow for cooling tower additives

** Includes softening chemicals water, 5 gpm

TABLE 9-4. VALUES ASSUMED FOR PRELIMINARY DESIGN CALCULATIONS

Cooling water pH 7.0

Cooling water total alkalinity = 75 ppm $CaCO_3$

Q_A = 1 gpm

Q_C = 5 gpm

Q_W = 10 gpm

$C_W(SiO_2)$ = 200 mg/L

$C_T(SiO_2)$ = 40 mg/L

$C_T(Ca)$ = 50 ppm $CaCO_3$

$C_T(Mg)$ = 20 ppm $CaCO_3$

$C_T(M.Alk)$ = 25 ppm $CaCO_3$

system at Bakersfield. A total of four alternative softening processes were evaluated using lime or caustic soda to raise pH and H_2SO_4 or CO_2 to neutralize softener effluent. The scale component limiting softener flow with sulfuric acid in use was SiO_2. When uing CO_2 for neutralization $CaCO_3$ limited softener flow, requiring use of much large softeners. Based upon a consideration of operating and capital costs, the option using NaOH and H_2SO_4 was found to be best for TOSCO. Only those calculations for the NaOH-H_2SO_4 case will be considered in this report.

The values calculated for preliminary design of the TOSCO plant are summarized in Tables 9-3 through 9-5. The water balance obtained for the TOSCO plant is shown in Table 9-1. Values that were assumed for these calculations are shown in Table 9-4. The blowdown from cooling towers 1-4 is the flow to the sidestream softener. As shown in Table 9-3, a blowdown flowrate of 165 gpm was required to maintain silica below 200 ppm in the cooling water. An effluent silica concentration of 40 ppm was estimated for the 40-C softener based upon prior experience. The total softener flowrate was 240 gpm. Estimated water quality for cooling water and softener effluent are shown in Table 9-5. These data explicitly show the level of removal expected in the softener for scale forming chemicals. Data for consumption of softening chemicals and sludge production are presented in Table 9-5. These data show that it was found necessary to add $MgSO_4$to aid in removal of SiO_2. If additional magnesium had been present in the well water this may not have been required.

A schematic diagram of the process design for the sidestream softeners is shown in Figure 9-2. This figure also shows the sizes recommended for major process components. The loading factors used for design of the settlers and filters are shown in Table 9-6. The overflow rate used for clarification, 0.9 gpm/ft^2 (1300 gpd/ft^2)is within the range normally encountered for lime softening systems. Actual settling data collected from earlier studies were used to estimate the overflow rate. A solids flux technique, using data supplied from previous studies, indicated that underflow should be in the range of 6% solids for the 20 ft. diameter reactor clarifiers recommended. Two parallel softeners were recommended to provide flexibility in operations. Each softener was designed to handle the full softener flowrate of 245 gpm. A depth of 15 ft. was recommended, based upon previous experience. The filter loading of about 6.0 gpm/ft^2 was selected as being reasonable for mixed media pressure filters. This value is well within the range typically used for waters of fairly low turbidity. Again, two parallel filters were recommended to permit continuous process operation during backwash cycles.

As noted previously, the concentration of silica in the cooling determines softener design for the chemical treatment selected, i.e., NaOH and H_2SO_4. Based on heat exchanger temperatures at the TOSCO refinery it was recommended that the SiO_2 concentration in cooling water be maintained at a maximum of 200 mg/L. A SiO_2 concentration of 40 mg/L in the softener effluent was considered feasible, based on prior operating experience with sidestream softening systems. Since $MgSO_4$ addition was recommended, the dosage could be increased to improve SiO_2 removal. The calculated detention time in the recommended solids contact clarifiers was about 2.5 hr. This

TABLE 9-5. PROJECTED WATER QUALITY DATA

Item	Temp.	Ca*	MG*	M.Alk.*	SiO_2	Cl	SO_4	Na	pH	TDS
Cooling Water	50°	860	280	75	200	1524	6465	3536	7.0	12,200
Softener Effluent	50°	50	20	25	40	1100	4690	2909	6.2	8,800

*Concentration units of ppm $CaCO_3$. All other values are in mg/L.

TABLE 9-6. DESIGN LOADING FACTORS

Item	Value
Softener Overflow Rate	0.9 gpm/ft^2
Filter Hydraulic Loading	6.3 gpm/ft^2

should provide sufficient capacity for precipitation, clarification, and sludge thickening. A sludge recycle rate of 20% was also recommended. This high recycle rate was recommended due to the presence of "inert" solids in the softener. Use of the softeners to clarify TCC scrubber blowdown introduces these "foreign" solids that may be less effective for softening than solids produced through precipitation. The preliminary process design, as shown in Figure 9-2, was accepted by TOSCO management and plans were made for final design and construction. The final design will be described in the next section.

FINAL PROCESS DESIGN

Final plans and specifications were developed for the TOSCO sidestream softener. These plans were based upon preliminary design calculations and recommendations. During the final design process, preliminary calculations are first double checked and corrected, if necessary. Vendor recommendations are also included for key process steps such as the solids contact clarifiers and mixed media pressure filters. These steps commonly require changes in flow, composition, and/or equipment siting during final design. During preliminary design, a process schematic is typically used with no concern for actual plant site layout. For final design, the physical layout of the entire plant site is reviewed and the most economical routing of new pipelines and new equipment layout should be determined. This review would consider aspects such as available pipe racks, physical location of process vessels, and available pressure and/or elevation for each flow. Such a design review may lead to changes in the process flow pattern anticipated during preliminary design. The results of the final process design will be described in this section. A comparison between preliminary and final designs will also be presented. Because the final design accurately describes the actual TOSCO plant, this comparison will be important when considering actual versus predicted process performance.

A schematic diagram for the final process design is included as Figure 9-3. This diagram is very similar to the preliminary process schematic, Figure 9-2. For the final design, boiler blowdown was added to the filter backwash tank rather than to the splitter box as shown in Figure 9-2. This change has no effect on softener performance or water quality. The chemical feed point for $MgSO_4$ was changed from the splitter box as originally proposed to the softener feed well. This change is an improvement since it increases the flexibility of operatio, i.e., magnesium feed can be adjusted invididually for each softener. Another change to be noted is the change in solids recycle rate for the solids contact clarifiers. The final design recommends a recycle ratio of 10% whereas a 20% ratio was recommended earlier. The maximum recycle ratio for final design is 16.7% of design flow. While solids recycle is below initially proposed levels, the rate used for final design was probably recommended by the supplier of the solids contact clarifiers, Infilco-Degremont. Their extensive experience in water treatment would ensure the final design values are reasonable. The final design also added supernatant return from the softener sludge pond. The only other change noted in the final design concerns the neutralization and filter feed tanks. These tanks were combined in a single vessel with a separating weir in the final design. The obvious reason for this change is a reduction in capital cost. None of the changes made in the final process flow scheme would change the accuracy of the preliminary design calculations. The reduced sludge recycle rate would limit the maximum solids concentration attainable in the softening reactors. This may reduce precipitation rates, leading to a less stable effluent, but this potential problem should be very insignificant.

In Table 9-7 the flow data used for preliminary and final design are compared. These data show that the major influent streams are the same for preliminary and final design. For the final design, provision was made for return of sludge lagoon supernatant and filter backwash. The flowrate needed for treatment chemicals in final design was 3 gpm less than that assumed during preliminary design. The net result of these changes is that flowrate through the softener for final design is 2 gpm higher than in the preliminary design. Sludge recycle is also lower in final design, as discussed previously. The estimated waste sludge flowrate was reduced from 10 gpm in preliminary design to 6 gpm for the final design. Considering all changes in flow for the final softener design, the end result is that treated water returned to the cooling system is 6 gpm higher than preliminary estimates. These changes are not great enough to cause a major loss of accuracy in preliminary calculations.

Water quality estimates are compared for preliminary and final design in Table 9-8. These data show that the preliminary water quality estimates described earlier were sufficient for final design purposes. A more detailed description of projected water quality data is presented in Table 9-5. The preliminary calculations for cooling water quality were also used for initial selection of treatment chemicals for the cooling system. Recovery of cooling tower blowdown enabled the chromate-zinc corrosion inhibitor system to be increased to 30-40 ppm CrO_4 and 3-5 ppm zinc. It was also recommended that cooling water pH be maintained in the range of 6.8 to 7.3 rather than 6.5-7.0 as had been done previously. A polymaleic acid (PMA) scale inhibitor was recommended for use in the cooling water. Experience with USS Chemicals has shown that PMA does not significantly interfere with sidestream softener operations. A wetting agent was also recommended for use in the cooling tower. Biological treatment recommended for the TOSCO plant was continuous chlorination with a 0.2-0.5 ppm free chlorine residual. The softening chemical requirements and sludge production rates are compared in Table 9-9. Again, preliminary calculations were directly used for final design.

The data of Table 9-10 compare preliminary and final design data for softening equipment. As shown in Table 9-10, preliminary estimates for many of the less important items were omitted. The only significant changes in equipment recommendations were the modest size increases for the solids contact clarifier and mixed media pressure filters. The reactor-clarifier diameter was increased from 20 ft. to 22.5 ft., while the depth was decreased from 15 ft. to 14 ft. for the final design. These changes may have been made to accomodate standard production models from the supplier. However, this increase changes design total hydraulic residence time from about 2.3 hr. to near 2.7 hr., an increase of 17%. This change should

TABLE 9-7. COMPARISON OF PRELIMINARY AND FINAL FLOW DATA

Item	Preliminary Design	Final Design
Boiler Blowdown	50 gpm	50 gpm
TCC Scrubber Blowdown	25	25
Filter Bakcwash Return	3	0
Sludge Lagoon Supernatant	2	0
Blowdown, CT Nos. 1-4	165	165
Treatment Chemicals, Total	2	5
Softener Flowrate	247	245
Sludge Recycle Flowrate	24.5	49
Waste Sludge Flowrate	6	10
Treated Water Flowrate	241	235

TABLE 9-8. COMPARISON OF PRELIMINARY AND FINAL WATER QUALITY ESTIMATES

Item	Preliminary Design	Final Design
Cooling Water pH	7.0	7.0
Cooling Water Temperature	50° C	50° C
Cooling Water TDS	12,200 mg/L	12,200 mg/L
Treated Effluent pH	8.2	8.2
Treated Effluent Temperature	-	-
Treated Effluent TDS	8,800 mg/L	8,800 mg/L
Treated Effluent TSS	-	2 mg/L

TDS = Total Dissolved Solids
TSS = Total Suspended Solids

TABLE 9-9. COMPARISON OF PRELIMINARY AND FINAL CHEMICAL CONSUMPTION

Item	Preliminary Dosage (ppm)	Design Consumption (lb/day)	Final Dosage (ppm)	Design Consumption (lb/day)
Anionic Polymer	-	-	0.5	1.5
$MgSO_4$	260	750	50	150
Na_2CO_3	380	1,100	380	1,100
NaOH	340	1,000	340	1,000
H_2SO_4 for Softener	49	144	49	144
Sludge Production	-	4,240	-	4,240

All values are based on average flow conditions.

TABLE 9-10. COMPARISON OF PRELIMINARY AND FINAL EQUIPMENT SIZING

Item	Preliminary Design	Final Design
Splitter Box	1000 gal	500 gal
Softener Diameter	20 ft	22.5 ft
Softener Depth	15 ft	14 ft
Waste Sludge Sump	-	3,300 gal
Neutralization/Filter Feed Tank	-	7,125 gal
Filter Backwash Holding Tank	-	12,000 gal
Filter Backwash Clear Well	-	8,000 gal
Filter Diameter	7 ft	7.5 ft

increase both reaction time and clarification capacity, providing an effluent of higher quality. The overflow rate for the clarifier was decreased from about 0.89 gpm/ft^2 (1150 gpd/ft^2) to about 0.65 gpm/ft^2 (936 gpd/ft^2 or about a 19% increase in area. The data comparing filter diameters also shows that the final design recommended larger filters. The filter loading used for preliminary design was 6.1 gpm/ft^2 while the loading for final design was 5.4 gpm/ft^2. This represents a decrease in filter loading of about 11%. As expected, the final design is more conservative than the preliminary design. The increases to major equipment siting appear to be in the range of 10 to 20%. However, these increases are moderate and appear reasonable. Increased size for softeners and filters should improve process performance, capacity, and flexibility of operation.

The final design used for the wastewater recycle/sidestream softening system was nearly identical to the preliminary design. No significant changes were made to the process flow scheme. All chemical calculations for the preliminary design were used for final process design and to select a suitable cooling water treatment system. Modest increases were made in the size of the softening reactors and final filters. These increases should not significantly affect water quality estimates. The changes made to the preliminary design should only serve to improve overall process performance and reliability.

As a final note to the process design section, the "degree of conservativeness" applied will be briefly considered. During design of a process such as sidestream softening, several opportunities are available for engineers to use conservative estimates of important parameters. This is true for plant engineering staff providing input design data and for the design engineer estimating unknown parameters. It is also common practice for design engineers to use a safety factor as a multiplier for initial size estimates for process equipment. These factors may be as large as 1.5. Furthermore, when used for clarifier design some engineers may apply the safety factor to area while others may apply it to diameter. Unless an effort is made to control these effects it is relatively easy for a process design to become excessively conservative. For the TOSCO design, it was endeavored to limit the tendency to "play it safe", since an economical design was explicitly requested. Judgments concerning process sensitivity and uncertainty were used as a guide for estimation of unknown quantities required for design. It was also endeavored to provide broader process flexibility to compensate for uncertainty in process efficiencies. For example, a broad range of feed rates for $MgSO_4$ can be used to offset a low SiO_2 removal efficiency. The process design recommended to TOSCO was not considered a conservative one. The provisions for process flexibility and redundancy of key process units were included as alternatives to strongly conservative assumptions and design.

PERFORMANCE OF TOSCO ZERO BLOWDOWN SYSTEM

Shortly after the final process design was completed and approved, a contract was let to begin construction. The sidestream softening/wastewater recycle plant was completed early in 1982. Operation of the plant commenced

March 18, 1982. Startup of the softening process went very smoothly. All softening chemicals recommended in the preliminary design were used during softener startup. After about one week, the newly constructed softening plant was lined out and operating well. During startup, TCC scrubber and boiler blowdown streams were being fed to the softener system. In this section the actual performance of the TOSCO softening system will be reviewed. Measured performance will be compared to performance predicted during preliminary design. These data will provide a convenient case for evaluation of the techniques used for softener design. Finally, the economic benefits accrued from wastewater recycle will be briefly reviewed.

COMPARISON OF PREDICTED AND ACTUAL PERFORMANCE

In the previous section, it was shown that no significant process changes were made during final design. Thus, the basic premises used for performance calculations should be applicable to the actual plant. However, during process design it was endeavored to provide sufficient operating flexibility in the softening plant to enable different modes of operation. In this regard, each softener unit was sized to handle the design flowrate and provisions were made to allow a fairly wide range of chemical feed rates. These provisions allow actual influent flowrates to be varied when both softeners are in operation. Also, a variety of influent chemical compositions could be handled by varying individual chemical feed rates. Operating flexibility must be included in process design because actual water quality is rarely identical to the quality used for design purposes. Furthermore, chemical calculations presume equilibrium conditions which cannot be attained in actual operation. Thus, actual process operations can be quite different from conditions assumed during process design. Such differences can lead to a large discrepancy between actual and predicted performance. For these reasons the actual operating conditions will first be compared with conditions used for design. These factors will be considered when predicted versus actual performance data are contrasted.

ACTUAL VERSUS DESIGN OPERATING CONDITIONS

Several factors may cause a process operator to alter conditions assumed to exist during process design. Plant expansions or modifications can alter conditions known at the time process design was undertaken. Economic conditions can have a strong influence over refinery operations, as can the nature of feedstocks. Changes in refinery operations may alter heat exchanges temperatures. These temperatures are of primary importance for setting cooling water limits for scale forming species. In plants like TOSCO using groundwater supplies, the quality of the wellwater is also likely to change with time. Changes in quality of cooling water makeup can cause very significant changes in softener flowrate and chemical dosage rates.

The data of Table 9-11 present a comparison between operating conditions actually in use at the TOSCO plant and those used for design. Perhaps the most important items listed in Table 3.1 are the flowrates for the cool-

TABLE 9-11. COMPARISON OF DESIGN ESTIMATE AND ACTUAL OPERATING DATA

Item	Design Estimate	Actual
pH	10.4	10.1 - 10.8
Q_s	165 gpm	215 gpm
NaOH	340 mg/L	180 mg/L
Na_2CO_3	380 mg/L	125 mg/L
$MgSO_4$	260 mg/L	230 - 260 mg/L
Softener Feed	245 gpm	130 - 1500 gpm (Avg 305 gpm)

All dosages are in mass units for chemical noted, 100% purity.

ing tower sidestream, Q_s, and softener feed. The actual flowrates are generally higher than values used for design. The sidestream flowrate from the cooling tower system was increased by an average of about 50 gpm (30% of design). This was done to reduce concentrations of scale component within the cooling water. Actual softener feed rates encompass a rather wide range, both above and below the design rate of 245 gpm. The upper limit on feed rate of 1500 gpm was not used routinely, but was done during upset conditions within the cooling towers. As usual, blowdown is used to control cooling water quality. The design included two parallel process trains with a stated capacity of 490 gpm when both trains were in use. The anticipated effect of the increased flowrate through the softeners is to decrease the quality of softener effluent and to maintain lower levels of scale chemicals in the cooling water.

The softener pH data of Table 9-11 shows that actual practice was based upon design recommendations. Control systems for chemical feed typically operate over a band of concentrations. The design pH of 10.4 is near the center of the actual pH range. However, the actual dosage for NaOH and Na_2CO_3 are well below design dosages. The reduced dosage reported for NaOH is primarily due to maintenance of lower alkalinity in cooling water, as will be discussed in a later section of this chapter. However, actual soda ash dosage is well below the design level. The recommended soda ash dosage was based upon maintaining equal molar concentratoins of calcium and total carbonate species in the softener, assuming all influent alkalinity would be converted to carbonate. The TOSCO plant was not operated in this manner. Because soda ash is a relatively expensive chemical, its dosage was reduced to improve process economy. Actual operation does not provide stoichiometric carbonate concentrations. Since there is an excess of calcium hardness in actual softener operations, actual effluent hardness should be higher than levels anticipated during process design.

The data of Table 9-11 show that the estimated dosage for $MgSO_4$ is very close to the dosage used in actual operation. However, hardness levels in the wellwater used for cooling tower makeup were lower than used for preliminary design estimates. Wellwater hardness in 1982 had fallen to 42 ppm calcium hardness (ppm $CaCO_3$) and 4 ppm magnesium hardness (ppm $CaCO_3$). As shown in Table 9-1, during preliminary design it was assumed that calcium hardness was 100 ppm $CaCO_3$ and magnesium hardness was 33 ppm $CaCO_3$. Based upon current makeup water quality, the estimated $MgSO_4$ dosage would be higher than actual dosage. This comparison shows that the design approach leads to a conservative estimate of $MgSO_4$ addition for removal of silica in the softener. However, the data also show that the method for dosage for $MgSO_4$ can be calculated with acceptable accuracy.

ACTUAL VERSUS ESTIMATED WATER QUALITY DATA

The previous discussions have provided the background for a comparison of predicted and actual water quality data. These data are presented in Table 9-12. Comparisons are presented for both softener effluent and cooling water composition. The accuracy of water quality estimates for each stream will be discussed. When necessary, information previously discussed will be used to better understand these comparisons.

The data for effluent from the softener are compared in Table 9-11. Except for the differences noted for both Ca and Mg hardness, the agreement between estimated and actual data is excellent. As shown by these data, actual removal of Ca and Mg is significantly less than anticipated. It was noted earlier that softener effluent hardness estimates were based upon jar tests conducted on a synthetic water. The values used, 50 ppm $CaCO_3$ Ca hardness and 20 ppm $CaCO_3$ mg hardness, were deemed optimistic but possible based upon prior experience with similar softening systems. Calcium removal is directly related to the dosage of soda ash. It was also noted that soda ash addition was reduced to improve operating costs for the softener system. With soda ash addition less than the stoichiometric amount effluent Ca hardness would be expected to increase. Furthermore, higher hardness levels in softener effluent would also cause the blowdown rate from the cooling water system to be higher than predicted. This would result in reduced hydraulic residence time in the reaction zone and resultant poorer removal efficiency. It should also be noted that a polymaleic anhydride precipitation inhibitor was added to the cooling water to control scale formation. Although this inihibitor has been found to provide minimal interference with precipitation softening operations, its presence may reduce removal efficiency for Ca and Mg. Actual Mg removal for softener effluent was closer to the predicted value than Ca removal.

A comparison of the remaining data for softener effluent shows excellent agreement for the remaining components. Silica removal was very close to predicted values. The design value of 40 mg/L SiO_2 was based upon prior experience. This verifies the effectiveness of magnesium salt addition for silica removal. The actual effluent pH is higher than anticipated, contributing to the discrepancy noted for alkalinity and sulfate concentrations. The agreement for the components other than Ca and Mg are well within an accuracy limit of 10%.

Data showing estimated and actual cooling water quality are included in Table 9-12. These data show that predicted quality was reasonably close to actual quality, but agreement was not as good as for softener effluent data. All estimated data were higher than actual. The primary reason for this discrepancy was the decision to maintain lower concentrations of scale forming species in the cooling water. As noted previously, this was accomplished by increasing the rate of blowdown to the softener system, resulting in a higher than predicted overall removal rate for Ca, Mg, and SiO_2. The primary reason for this was to reduce Ca concentrations to avoid potential problems with gypsum ($CaSO_4$) scale formation. Insufficient information on actual operation was available to permit calculation of actual cycles of concentration. The design concentration factor was about 42, however.

Detailed analytical data could not be obtained for wellwater and the other feed streams, TCC scrubber blowdown and boiler blowdown. Thus, it is difficult to ascertain the actual reasons for the discrepancies between actual and predicted cooling water quality. The reduced alkalinity in actual cooling water is due to the slightly reduced pH used for actual operation. This reduced alkalinity also decreased actual NaOH dosage, contributing to lower Na levels in the cooling water. The worst prediction was for

TABLE 9-12. COMPARISON OF ESTIMATED AND ACTUAL WATER QUALITY DATA

pH	8.2	8.5	7.0	6.2-6.7
Ca Hardness (ppm $CaCO_3$)	50	280-400	860	520-700
Mg Hardness (ppm $CaCO_3$)	20	16-120	280	170-200
Na^+ (mg/L)	2,900	2,793*	3,540	2,900-3,200
M.O. Alkalinity (ppm $CaCO_3$)	25	35	75	20-40
Cl^- (mg/L)	1,100	1,200	1,525	1,200-1,500
$SO_4^=$ (mg/L)	4,700	4,500	6,470	4,650-5,500
SiO_2 (mg/L)	40	42	200	130-150
TDS (mg/L)	8,800	8,700	12,250	10,400

*Na^+ concentration was estimated to provide electroneutrality.

TABLE 9-13. ESTIMATED ANNUAL COST DATA

Item	Annual Savings	Annual Cost
Wellwater Consumption (300,000 gal/day @ 33c/1000 gal)	$ 36,000	
Disposal Well Operating Cost (maintenance, etc.)	300,000	
Reduced Chromate Consumption	70,000	
Disposal Well Tax Reduction	365,000	
	$771,000	
Softening Chemicals		110,000
Operating Labor (3 men per day @ $30/hr)		263,000
Softener Maintenance		100,000
Estimated Net Cost Reduction $298,000		$473,000

sulfate, which was about 1400 mg/L too high. The reason for this is unknown, but may be due to actual wellwater alkalinity being lower than anticipated. It was noted previously that makeup water quality had changed for both Ca and Mg hardness. The chloride ion prediction appears to be quite good, but preliminary estimates did not include contributions from cooling water chlorination. Inclusion of chlorine feed in design calculations would have increased the predicted value for Cl. However, it is also possible that actual drift losses were greater than the preliminary design estimate of 53 gpm.

Overall, design predictions were sufficiently close to actual data for both softener effluent and cooling water quality to permit a realistic assessment of softener performance and need for chemical treatment of cooling water. Predicted data were generally higher than actual data. This would lead to conservative estimates of the impacts of softener operation on the cooling water system. While excessive conservatism is undesirable, the data of Table 9-11 show a moderate level of conservatism for most parameters. The data of Tables 9-11 and 9-12 show that careful application of design techniques described in this report provide excellent estimates of actual operating and performance data for sidestream softening systems.

GENERAL ASSESSMENT OF SIDESTREAM SOFTENER SYSTEM

The total cost for design and construction of the TOSCO sidestream softening system in 1982 was $3,500,000. The TOSCO system provided for recovery and reuse of cooling tower blowdown, boiler blowdown, and TCC scrubber blowdown. Recovery of these wastewater streams significantly reduced wastewater discharges at the Bakersfield refinery. Operating and management personnel were pleased with system design and performance. Careful planning and attention to detail during design and construction provided for an easy startup. Since actual performance was fairly close to predicted performance, there were no major "surprises" encountered during initial operation. The accuracy of predicted performance enabled adequate preparation for cooling water treatment and sludge disposal. Operating costs, due primarily to chemical additions and labor, were generally lower than anticipated. Actual economic benefits were accrued through operation of the softener/wastewater recycle system that reduced overall refinery operating costs. Cost reductions were achieved for wellwater supply, cooling water chemical usage, maintenance costs, and superfund taxes.

The primary objective of the sidestream softener system at TOSCO was to reduce wastewater production. This also leads to reduced demand for freshwater supply. Based upon actual operating data, wellwater consumption at the Bakersfield refinery was reduced by a minimum of 300,000 gal/day after the softener system was placed on-line. This led to estimated annual savings of about $36,000, as shown in Table 9-13. The very high unit cost of $0.33/1,000 gal includes power costs, well maintenance, and taxes on groundwater usage. As noted previously, local and state government used these taxes to increase incentives to reduce fresh water consumption. This situation is unique because of the semi-arid climate at the Bakersfield plant site.

Recovery and recycle of cooling tower blowdown also had an impact on consumption of cooling water treatment chemicals. The major changes noted in cooling water treatment were increased concentration for both chromate and Zn corrosion inhibitors. Chromate concentrations were nearly doubled, going from about 20 mg/L to 30-40 mg/L CrO_4 after startup of the softener. Zinc concentrations were approximately 2 mg/L prior to startup and 3-5 mg/L afterwards. The higher chromate concentration did not increase consumption of chromic acid since chromate is not removed during softener operation. The chromate is returned to the cooling tower with the treated effluent, effectively reducing chromate additions by recovery of cooling tower blowdown. However, at the alkaline conditions maintained in the softeners, zinc is removed as $Zn(OH)_2$ with the sludge. Consequently, addition of Zn to cooling water was increased by softener operation. These changes led to net savings for cooling water treatment chemicals of approximately $70,000 per year, as noted in Table 9-13. A potentially important cost increase could result from increased corrosion rates within the cooling water system. Generally, as the ionic strength of water increases the water becomes more corrosive. The high levels used for both chromate and zinc were intended to offset this effect. Measured corrosion rates at the TOSCO refinery using the standard coupon test increased from about 0.4 mils per year (mpy) prior to wastewater recycle to 0.7 mpy after recycling was implemented. Corrosion rates less than 1 mpy are generally considered acceptable for well operated open cooling tower systems (4,5,6). Thus, increased corrosion rates were not considered to represent an additional cost burden.

Prior to softener operation, blowdown streams from the cooling tower system, boilers, and TCC scrubber were disposed by deep well injection. Operation of their disposal well represented a very significant cost for the Bakersfield refinery. These costs include electrical power, maintenance, and taxes. Power consumption in disposal well operations is strongly influenced by the volume of wastewater injected. The injected wastewater must be forced through a porous sand in the disposal zone. This zone is subject to pluggage by solids remaining in the wastewater after filtration. Higher injection well flowrates increase both the pressure drop required to maintain well flow and the rate of buildup of pressure drop due to plugging. Both factors will have an impact on pumping efficiency for the injection well system. Higher rates of plugging also increase the frequency of well shutdown for cleanup operations designed to remove deposited solids. These factors show that injection well operating and maintenance costs do not increase linearly with wastewater flowrate; the incremental cost per unit volume of wastewater increases as flow increases. While it is difficult to isolate these costs, TOSCO personnel estimate that approximately $300,000 per year will be saved by recovery and re-use of wastewater previously injected. These data are included in Table 9-13.

The superfund taxes levied on disposal well operation represent a significant cost to the TOSCO refinery. These taxes are based on the volume of wastewater injected via disposal well. The TOSCO sidestream softening system reduced flow to the disposal well by about 170,000 gal/day. As shown in Table 9-13, TOSCO estimates that superfund taxes would be reduced by $365,000 per year due to recycle of wastewater streams. This represents an average tax rate of about $5.89 per 1,000 gal of wastewater. This presents a very strong incentive for reduction of wastewater generation rates. The data of Table 9.13 show that superfund taxes represent the single largest savings for softener operation. Disposal well cost reductions, consisting of maintenance and taxes, represent over 85% of total savings estimated.

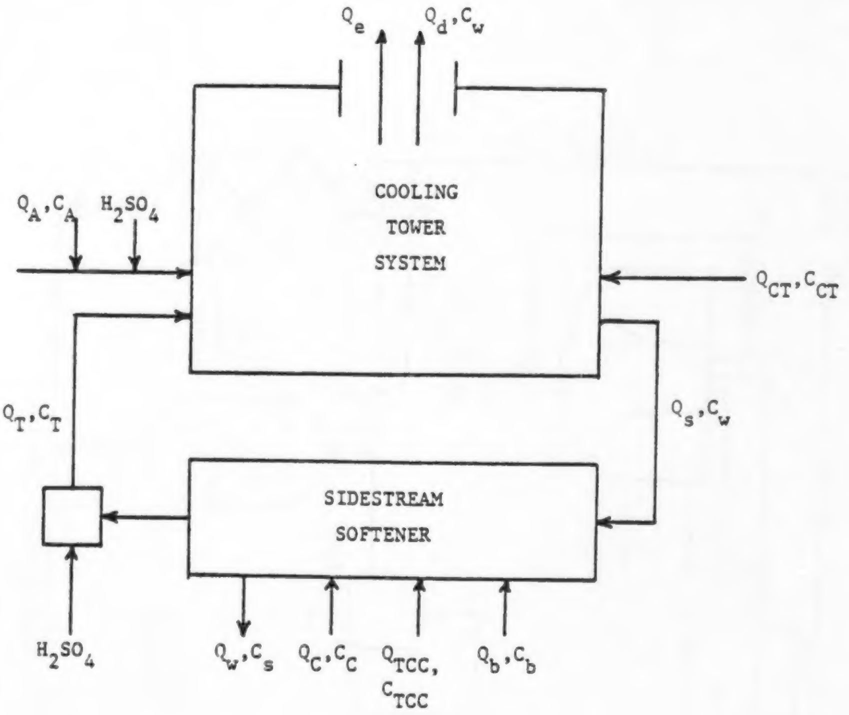
The increased plant costs for softener operation consist of softener chemical costs, operating labor, and estimated maintenance costs, as noted in Table 9-13. Actual softener chemical costs of about $110,000 per year were estimated, based upon initial softener operations. Chemical costs estimated during process design were $135,000 per year. Softener operation required addition of one operator per shift, leading to an estimated annual cost of about $263,000. Although long term softener maintenance cost data were unavailable, TOSCO estimates annual maintenance costs at $100,000 resulting in a total cost increase of about $474,000 annually. Data concerning additional costs and benefits such as interest, property taxes, income taxes, and depreciation were not available to the authors. However, it is likely that these factors would increase the economic benefits attributable to softener operation.

The data of Table 9-13 show that the estimated total cost increase for softener operation was $473,000 annually while estimated annual cost reduction was $771,000. The net effect on refinery operating cost was a decrease of almost $300,000 annually. This net savings represent 8.6% of the total cost of plant design and construction. The TOSCO design provides an economic incentive for wastewater recycle in addition to the more general incentives for environmental protection and water conservation. Incentives for social concerns such as the two noted above are difficult to quantify in economic terms. The TOSCO case is unique in that both economic and social incentives favored construction and operation of wastewater recovery facilities. The data of Table 9-13 show that the economic incentive is mostly attributable to reduced tax burdens, however. In the absence of superfund taxes, annual refinery operating costs would have increased, but the increased cost would be minor.

RECOMMENDATIONS AND CONCLUSIONS

The design used for sidestream softening and wastewater recycle at the TOSCO refinery in Bakersfield, California, provided a reliable and cost effective system. The design technique used for preliminary process design presented an accurate, well defined picture of actual process performance. This design technique is obviously well suited for sidestream softener process calculations when applied in a conscientious manner. Preliminary calculations can be used to assess potential impacts of softener operations on the overall plant with a high degree of confidence. The design technique can also be used to investigate different treatment chemical combinations with the objective of selecting the lowest cost alternative. Such a review for the TOSCO plant led to selection of caustic soda rather than lime to elevate pH in the softeners. Each plant site is unique, however, and different conditions may result in a different recommended chemical treatment scheme.

Further work is necessary to improve predictions for removal of hardness in sidestream softeners. Prediction of effluent hardness was quite poor for the TOSCO design. This work should include consideration of effects of scale inhibitors on softener performance. Because several scale inhibitors can strongly influence precipitation kinetics, their presence can degrade softener performance. The situation is further complicated by the multiplicity of scale inhibitors available for use in cooling waters. The isotherm method used to predict silica removal is well suited for design of sidestream softeners, however.


Q_e
Q_d, C_w
Q_A, C_A
H_2SO_4
COOLING
TOWER
SYSTEM
Q_{CT}, C_{CT}
Q_T, C_T
Q_s, C_w
SIDESTREAM
SOFTENER
H_2SO_4
Q_w, C_s
Q_C, C_C
Q_{TCC},
C_{TCC}
Q_b, C_b

LEGEND

Q_e = Evaporation Loss
Q_d = Drift Loss
Q_m = Make-up Flow Rate
Q_A = Additive Flow Rate
Q_{CT} = No. 5 Cooling Tower Blowdown
Q_S = No. 1-4 CT Blowdown
Q_b = Boiler Blowdown
Q_{TCC} = TCC Scrubber Blowdown
Q_C = Softener Chemical Feed Rate
Q_w = Waste Sludge Flow Rate
Q_T = Treated Water Flow Rate

FIGURE 9-1 SIDESTREAM SOFTENING SYSTEM SCHEMATIC DIAGRAM

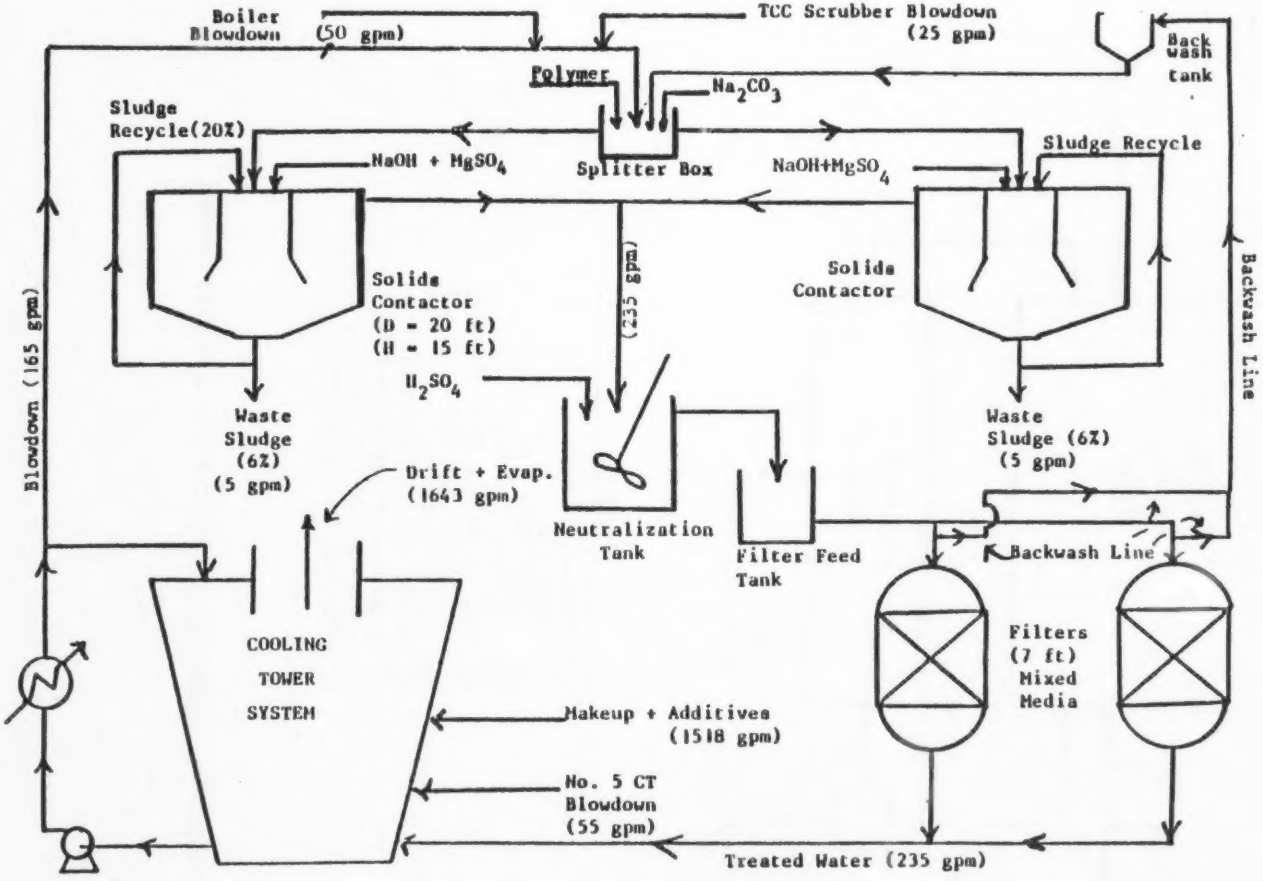

Boiler Blowdown (50 gpm)
TCC Scrubber Blowdown (25 gpm)
Back wash tank
Polymer
Na_2CO_3
Sludge Recycle(20%)
NaOH + $MgSO_4$
Splitter Box
NaOH+$MgSO_4$
Sludge Recycle
Solids Contactor (D = 20 ft) (H = 15 ft)
(235 gpm)
Solids Contactor
Backwash Line
H_2SO_4
Waste Sludge (6%) (5 gpm)
Waste Sludge (6%) (5 gpm)
Blowdown (165 gpm)
Drift + Evap. (1643 gpm)
Neutralization Tank
Filter Feed Tank
Backwash Line
COOLING TOWER SYSTEM
Filters (7 ft) Mixed Media
Makeup + Additives (1518 gpm)
No. 5 CT Blowdown (55 gpm)
Treated Water (235 gpm)

FIGURE 9-2 PRELIMINARY DESIGN SIDESTREAM SOFTENING PROCESS SCHEMATIC

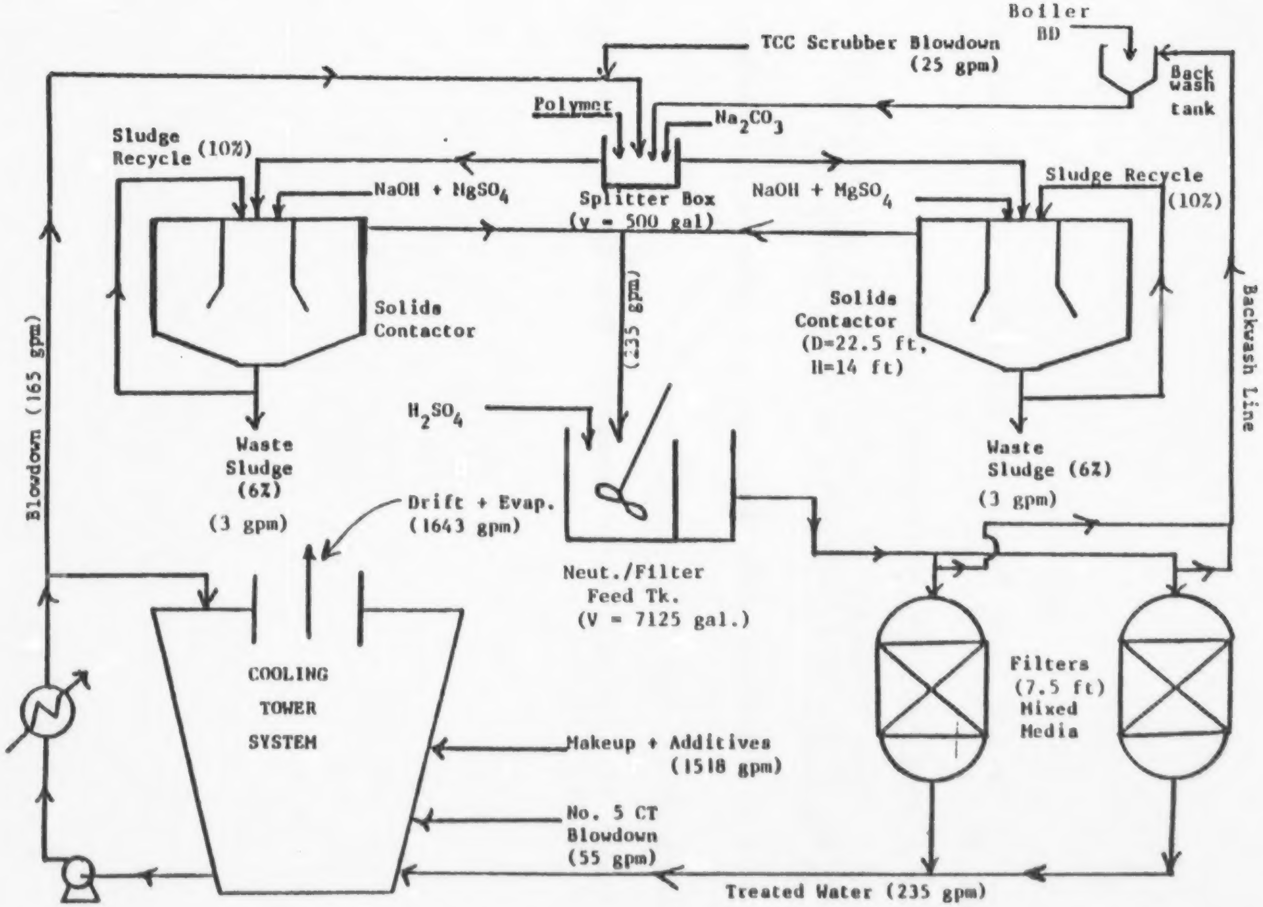

Boiler BD
Back wash tank
TCC Scrubber Blowdown (25 gpm)
Polymer
Na_2CO_3
Sludge Recycle (10%)
$NaOH + MgSO_4$
Splitter Box (V = 500 gal)
$NaOH + MgSO_4$
Sludge Recycle (10%)
Backwash Line
Solids Contactor
(235 gpm)
Solids Contactor (D=22.5 ft, H=14 ft)
H_2SO_4
Waste Sludge (6%) (3 gpm)
Waste Sludge (6%) (3 gpm)
Blowdown (165 gpm)
Drift + Evap. (1643 gpm)
Neut./Filter Feed Tk. (V = 7125 gal.)
COOLING TOWER SYSTEM
Filters (7.5 ft) Mixed Media
Makeup + Additives (1518 gpm)
No. 5 CT Blowdown (55 gpm)
Treated Water (235 gpm)

FIGURE 9-3 FINAL DESIGN SIDESTREAM SOFTENING PROCESS SCHEMATIC

References

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